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# Evaluation of Solid Sorbents for Water Sampling

Arthur D. Little, Inc.
Cambridge, MA

Prepared for

Industrial Environmental Research Lab.
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16. ABSTRACT The report describes a systematic evaluation of the applicability of macroreticular resins for general and compound-specific sampling of organics. The first portion is an extensive review of current pertinent literature concerned with the use of macroreticular resins for sampling and analysis of organic compounds in an aqueous matrix. The main body of the report describes and presents results of a laboratory investigation of selected solid adsorbents that appeared promising for sampling, based on the literature review. Results of screening a variety of sorbent-solute pairs indicate that a combination of two dissimilar resins is the most promising approach to a general purpose sorbent sampling system. In particular, a combination of XAD-2 and XE-347 resins offers the possibility of collection and recovery of both non-polar and polar organic species. This XAD-2/XE-347 system was, for the most part, found to be comparable with solvent extraction in regards to recovery; polar species such as phenols and pyrrole were recovered in higher yield from the cartridge.

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## SUMMARY

The qualitative and quantitative analysis of trace levels of organic compounds in aqueous industrial effluents has been the object of increasing interest and study. An attractive alternative to liquid-liquid extraction is the use of an *in situ* continuous extractive sampler containing a solid sorbent material. The Process Measurements Branch of the EPA's Industrial Environmental Research Laboratory in Research Triangle Park has sponsored a study of the feasibility of this approach to sampling for purposes of environmental assessment.

This report describes a systematic evaluation of the applicability of macroreticular resins for general and compound-specific sampling of organics. The first portion of the report presents an extensive review of the current pertinent literature concerned with the use of macroreticular resins for sampling and analysis of organic compounds in an aqueous matrix. The main body of the report describes and presents the results of a laboratory investigation of selected solid adsorbents that appeared promising for sampling based on the literature review.

The basic approach used in this work was the generation and analysis of the frontal breakthrough curve produced by challenging a sorbent cartridge with an aqueous solution of organic analyte at constant flow rate. Using this approach, the volumetric capacity ($V_{50}$), a quantitative measure of the breakthrough characteristics of the sampling decice, was determined.

The adsorption and desorption processes involved in the sampling and analysis procedure were examined separately. Adsorption was studied by the generation of breakthrough curves, while recovery was examined by recovery experiments under conditions where no breakthrough occurred. This chromatographic approach to characterization of sorbent-solute behavior allowed rapid, simple quantitative evaluation of resins for water sampling applications. $V_{50}$ has been shown to be a fundamental property of the sorbent-solute system. At low ($\leq$10 ppm) solute concentrations, a 10 ppb solution can be expected to breakthrough a given sorbent cartridge just as rapidly as a 10 ppm solution does. A reduced breakthrough capacity due to weight capacity limitations is observed at concentrations of 100 ppm or higher.

Values of $V_{50}$ determined in small-scale laboratory experiments were valuable in setting design parameters for a full-scale sampling cartridge. The use of such screening studies is highly recommended whenever it is desired to determine the optimum sampling system for a particular organic analyte in water.

Uptake is greatly affected by the flow rate through the cartridge. To ensure equilibrium uptake, the flow rate must be such that the face velocity (sample flow rate in mL/min divided by the cross-sectional area of the resin bed) is $\leq$4 cm/min. This constraint combines with $V_{50}$ to determine the size and shape of resin bed required for any particular sampling application.

Based on the results of screening a variety of sorbent-solute pairs, it appears that a combination of two dissimilar resins is the most promising approach to a general purpose sorbent sampling system. In particular, a combination of XAD-2 and XE-347 resins offers the possibility of collection and recovery of both non-polar and polar organic species. This XAD-2/XE-347 system was, for the most part, found to be comparable with solvent extraction in regards to recovery; polar species such as phenols and pyrrole were recovered in higher yield from the cartridge.

## II. INTRODUCTION

The qualitative and quantitative analysis of trace levels of organic compounds in aqueous industrial effluents has been the object of increasing interest and study. Current EPA sampling and ananysis procedures for organics are directed towards comprehensive characterization, as in Level 1 (32), or towards specific compound quantification as in Level 2 (26), or in priority pollutant analysis (17, 18). Liquid-liquid extraction with an immiscible organic solvent is the approach that has been most widely used for isolation of organics. This approach is capable of giving quantitative recovery of a wide range of non-polar organic materials. On the other hand, transport and extraction of large volumes (1-10L) aqueous samples, required to meet detection limit constraints, is cumbersome and frequently complicated by the formation of emulsions. Furthermore, very polar, water-soluble organic species are not always extracted efficiently.

An attractive alternative approach for collection of organics from large quantities of water is the use of an *in situ* continuous extractive sampler containing a solid sorbent material. An early device of this type, once widely used in the field, was the EPA's carbon adsorption module (CAM)(53). A number of previous workers had investigated other sorbent media including macroporous resins (28, 29, 51, 52, 58, 59), ion exchange resins (45) and polyurethane foam plugs (40). Based on information available in the literature, it appeared that sorbent approaches offered potential advantages over solvent extraction by a number of criteria:

1. Convenience: A compact sorbent cartridge is more easily handled and shipped than a large volume aqueous sample.

2. Sample Integration: A sorbent approach is inherently compatible with time-integrated sample collection while solvent extraction is more commonly associated with grab or composite/grab aqueous samples.

3. Range of Applicability: Sorbent approaches appear to be suited for ppm and lower levels of organics. Solvent approaches are good for ppm or higher levels.

4. Recovery of polar organics: A sorbent approach can potentially be tailored to allow good recovery of polar organics as well as hydrophobic species.

This report describes and presents some results of a systematic laboratory investigation of the applicability of macroreticular resins for general and compound specific sampling of organics, based on small scale, chromatographic experiments. The objective was to develop screening procedures and a data base that would allow selection of the resin(s) best suited to a particular sampling application and selection of a sampling module size/configuration that gives quantitative collection of contaminant(s) from the aqueous stream of interest.

The basic approach used in this work was the generation and analysis of the frontal break through curve produced by challenging a sorbent cartridge with an aqueous solution of organic analyte at constant flow rate. This methodology has been described in some detail elsewhere (19, 24). The approach, which has also been successfully applied to air sampling systems (1, 19, 44), involves determination of the volumetric capacity ($V_{50}$) of the sorbent for the specific pollutant. The volumetric capacity is a quantitative measure of the breakthrough characteristics of the sampling device and is the maximum volume of sample stream that can be pulled through the resin while still retaining the pollutant. The units of $V_{50}$ are mL (of aqueous sample) per cc (of resin bed).

A principal focus of this study was the design of sorbent systems appropriate for sampling of industrial effluents, which generally contain parts per million (or higher) concentrations of organics. The experimental work was therefore carried out using solutions containing analytes at 10 ppm concentrations. This level is high enough to be realistic in terms of effluent sampling but also low enough so that the breakthrough is not limited by the weight capacity of the sorbent. The experimental results can therefore be applied to sampling of ambient concentrations (ppb levels) of organics in water as well as to industrial emissions (ppm levels).

Section III of this report presents a review of the literature on use of solid adsorbents for collection of organic species from water. The literature survey was broad, if not exhaustive, and was intended to provide an overview of the state of the art prior to this work. The experimental approach used in the current study is presented in Section IV. Section V includes results and discussions, while Section VI presents conclusions and recommendations.

## III. LITERATURE REVIEW

The analysis of trace levels of organic compounds in aqueous media has, of late, become the object of intense study. This body of literature has been surveyed to evaluate the state of the art of procedures for isolation and recovery of organic materials. The particular emphasis of the literature review, and of the discussion that follows, was placed on documenting what was known about the quantitative aspects of available extractive isolation procedures, using solvents and sorbents, for organic species in water. Criteria considered in evaluating the available methods included recovery, applicability to ambient or drinking water levels vs. industrial effluent levels, suitability for batch or continuous sampling, and convenience. The survey explicitly excluded coverage of the following: methods directed solely towards qualitative identification of species present in a given water type; methods related solely to vapor stripping/sparging of purgeable organics; methods based on evaporative concentration or freeze-drying of water; and methods from the older literature that have been adequately reviewed in secondary sources.

### A. Solvent Extraction

Liquid-liquid extraction with an immiscible organic solvent is the approach that has been most widely used for isolation of organics from aqueous environmental samples. This approach, which has its roots in the methodology of synthetic organic chemistry, is capable of giving quantitative recoveries of a wide range of non-polar organic materials. Systematic studies by, among others, Webb and co-workers (59, 60) at the EPA Athens, Georgia, Environmental Research Laboratory, have helped to define the strengths and limitations of this approach.

Solvent extraction is generally carried out as a batch operation on a collected water sample (which may, itself, represent grab, composite or continuous sampling of the aqueous stream concerned). The technique is conveniently applied to 1-10 L volumes of aqueous sample, using approximately 50-250 mL of organic solvent per L of sample for each extraction (27). The extraction can be done using separatory funnels or by vigorous, 10-24 hr, mixing of solvent and aqueous phase (27). A variation on these conventional procedures, known as microextraction, has also been used successfully for some applications. In micro extraction, a solvent:sample ratio of 1:100 and a total organic solvent volume of 100 µL to 1 mL is typically used (16). This procedure, which can only be used for solvents with very low water solubility, eliminates the need for concentration of the organic extracts prior to analysis.

In addition to batchwise extraction, developments have been reported in the use of continuous liquid-liquid extractors (30, 61, 63, 64). Suffett and co-workers (63, 64) have designed such an apparatus that uses a Teflon helix to mix the water and organic solvent. In addition, separation of the two phases and subsequent solute concentration and solvent recovery is accomplished automatically, "allowing for unattended continuous liquid-liquid extraction of large volumes" (64).

The extraction efficiency (recovery) achievable by a particular solvent extraction procedure is directly related to the tendency of the organic species of concern to selectively partition into the organic solvent from water, according to the general rule of "like dissolves like". The less polar the solute, the more tendency it will have to dissolve in the organic phase and thus be recovered; conversely, the more polar the solute, the lower will be its recovery. It is necessary to adjust the pH of the aqueous sample to $\geq 11$ for organic bases or $<2$ for organic acids in order to convert the organics to their unionized, less polar form for maximum extraction efficiency.

It is possible to predict the maximum achievable extraction efficiency for a given organic solvent and organic species of concern if the appropriate solvent-water partition coefficient for the species is known. Extensive listings of partition coefficients (and correlation equations for extrapolation to other solvent systems) are available (33), and these can be used to estimate extraction efficiencies for individual organic species. Table 1 lists partition coefficients for some easily extracted and poorly extracted compounds.

TABLE 1

Illustrative Values of Solvent: Water Partition Coefficients*

| Compound | $P_{CHCl_3: H_2O}$ | $P_{heptane: H_2O}$ | $P_{ether: H_2O}$ |
|---|---|---|---|
| Efficiently Extracted | | | |
| Propyl Ether | 580 | 34 | 18 |
| Hexyl Amine | 490 | 30 | 16 |
| Butyl Mercaptan | 1,200 | 98 | 34 |
| Benzene | 460 | 24 | 15 |
| Chlorobenzene | 6,200 | 1,100 | 150 |
| Indene | 78,000 | 1,500 | 180 |
| Acridine | 20,000 | 9,300 | 575 |
| Thiophene | 301 | 13 | 10 |
| Inefficiently Extracted | | | |
| Acetic Acid | 0.03 | 1.0 | 0.4 |
| Phenol | 2 | 0.05 | 31 |
| Benzene Sulfonic Acid | 0.0001 | 0.000006 | 0.002 |
| Ethylene Glycol | 0.002 | 0.00001 | 0.005 |

*Estimated using data bank and methods of reference 33.

Table 2 illustrates a comparison of some measured and calculated extraction efficiencies for several model compounds.

TABLE 2

Comparison of Calculated and Measured Extraction Efficiencies

| Compound | Solvent | % Recovery* | |
|---|---|---|---|
| | | Calculated | Measured |
| Napthalene | $CHCl_3$ | 99 | 96** |
| Phenol | $CHCl_3$ | 17 | 28** |
| p-Cresol | $CHCl_3$ | 60 | 67** |
| Dibenzofuran | $CHCl_3$ | 100 | 100** |
| Phenol | $CH_2Cl_2$ | 54+ | 75 |
| o-Chlorophenol | $CH_2Cl_2$ | 95+ | 111 |
| p-Nitrophenol | $CH_2Cl_2$ | 85+ | 95 |
| 2,4,6-Trichlorophenol | $CH_2Cl_2$ | 100+ | 112 |
| Phenol | $CH_2Cl_2$ | 17+ | 20 |
| Phenol | $CH_2Cl_2$ | 84 | 82 |

*ADL data except as noted.

**Data of R.G. Webb, Reference 59

+Calculated values are for chloroform.

## B. Adsorption on Carbon

Adsorption on Granular Activated Carbon (GAC) is widely recognized as an effective method for the removal of many classes of organic compounds from aqueous environments. This is accomplished by allowing the water sample to contact the GAC either in a static mode, by adding GAC to a volume of water and allowing equilibrium to take place, or in a dynamic mode, by passing the sample through a bed packed with GAC. For sampling applications, the dynamic mode is much more common than the static mode. Organic compounds are separated from the water by adsorption onto the surface of the carbon.

Braus et al., (5) used a simple iron pipe packed with activated carbon to adsorb organics from various surface water supplies of seven U.S. cities. Water was forced into the bottom of a 3-foot x 4-inch diameter cartridge at a flow rate of 0.1 to 0.6 gallons per minute. After passing the volume of water through, the cartridge was dismantled and the carbon was air-dried, then Soxhlet extracted with diethyl ether. These early (1950's) systems were intended to process large quantities of water in order to obtain sufficient sample for analysis by the methods of the time. For example, Middleton and co-workers (37) were able to isolate gram quantities of organics which they characterized as aliphatic and aromatic hydrocarbons, esters, aldehydes and ketones, by processing 2,000 to 10,000 gallon samples of Nitro, W. Va., waters. They calculated concentrations of 45 to 3000 ppb of carbon adsorbable/chloroform extractable organics in the river water. A similar carbon adsorption system (4-feet x 4-inch steel pipe) has been included as a tentative method of Standard Methods for the Examination of Water and Wastewater (63). The solvent to be used for extraction is specified as chloroform, giving a carbon chloroform extract (CCE) measurement. In addition to the CCE measurement, Buelow and co-workers (6) also report a measurement obtained by extraction of the previously chloroform-extracted carbon with 95% ethyl alcohol (CAE). Consistently higher measurements were obtained with this solvent, however, blank values were also consistently higher as well.

Other than these early reports, relatively few publications exist on the use of carbon as a sampling technique. This is largely due to recognition of some major sources of error in quantitative analysis of organics in water using carbon as an adsorbent. For example, Criswell and co-workers(11) observed low and erratic recoveries of model compounds at known concentrations in water using carbon (Filtrasorb 300, Calgon Corp., Pittsburgh, PA). The authors attribute some of the low recoveries to significant breakthrough of particular analytes during sampling. Another characteristic problem with carbon is the difficulty in desorbing some compounds. Somewhat improved recovery can be achieved by the choice of solvent used to desorb analytes from GAC. In a continuous flow experiment, Pahl, Mayham and Bertrand (43) ranked ten solvents for their efficiency of removing phenol from carbon. Recoveries ranged from 0.6% using water to 27% using dimethylformamide. Both breakthrough and desorption difficulties can lead to substantial underestimates

of the actual sample concentration when using the values obtained from carbon adsorption. Also, it is generally suspected, but not rigorously demonstrated, that chemical changes can occur on the surface of the GAC. Thus, qualitative as well as quantitative information could be in substantial error.

## C. Adsorption on Macroreticular Resins

Reports in the literature in recent years have shown a substantial interest in the use of macroreticular resins for sampling and analysis of organics in aqueous streams. These resins, of which Rohm and Haas's XAD-2 is perhaps the most commonly used, are synthetic polymeric materials with characteristically large pores and high specific surface area (Appendix B). Table 3 lists a number of types of resins that are available. These represent a wide range of chemical composition and thus provide the possibility of more selectivity and specificity than is available with carbon. Furthermore, it is generally acknowledged that macroreticular resins give consistently higher recoveries than carbon, for many types of compounds.

As with carbon, resin adsorption is usually achieved by passing the sample solution through a column packed with resin. Desorption of the analytes is then accomplished by either elution or Soxhlet extraction with a solvent, or, in some cases, by thermal desorption. Thermal desorption is usually applied only to those resins, such as Tenax-GC, which have especially high thermal stability. Solvent desorption approaches are much more common for the styrene-divinyl benzene (XAD-1, XAD-2, XAD-4) polyacrylate (XAD-7, XAD-8) and related synthetic resins.

Much of the pioneering work using XAD sorbents was carried out by Fritz and co-workers at the Department of Energy's Ames, Iowa, laboratories and by Webb and co-workers at EPA's Athens, Georgia, laboratory. For example, Webb (59) reported a systematic evaluation of the use of XAD-2, 4, 7 and 8 singly and in combinations, for overall recovery (uptake plus desorption) of model compounds in water. Table 4 presents some of his results (59).

It is apparent from these data that the XAD resins are suitable sorbents for the analysis of several non-polar compounds. This is consistent with observations that retention on styrene-divinylbenzene co-polymers appear to be governed mostly by hydrophobic forces (57). Recovery efficiency, understandably, crudely follows the same trend as solvent extraction using chloroform. The more polar compounds, though, present a substantial problem for these sorbents. Compounds such as phenol, which is a common pollutant, are recovered in particularly low yield. Also, mixed beds of various XAD resins appear to improve recovery only marginally over beds of single sorbents.

Fritz and co-workers have also played a substantial role in setting forth some of the operational and applications aspects of the use of XAD resins. For instance, they demonstrated (28) that essentially no change in recovery occurs over a concentration range of 50 ppb to 50 ppm, for non-dissociated solutes (Table 5).

TABLE 3

Macroreticular Resins Used for Sampling of Organics from Water

| Resin | Chemical Type |
|---|---|
| XAD-1 | Styrene-Divinylbenzene |
| XAD-2 | Styrene-Divinylbenzene |
| XAD-4 | Styrene-Divinylbenzene |
| XAD-7 | Acrylic ester |
| XAD-8 | Acrylic Ester |
| Tenax-GC | Phenylene Oxide |
| IRA-900 | Styrene Divinylbenzene, $R_4N^+$, Strong Anion Exchange |
| IRA-904 | Styrene Divinylbenzene, $R_4N^+$, Strong Anion Exchange |
| IRA-93 | Styrene Divinylbenzene, $R_3N$, Weak Anion Exchange |
| Amberlite 200 | Styrene Divinylbenzene, $SO_3^-$, Strong Cation Exchange |
| A-26 | $-N(CH_3)_3$ Strong Anion Exchange |
| IRC-50 | Methacrylic Acid Divinylbenzene, $SO_3^-$, Strong Cation Exchange |
| IRC-84 | Acrylic-Divinylbenzene, $COO^-$, Weak Cation Exchange |
| XE-340 | Carbonaceous |
| XE-347 | Carbonaceous |
| XE-348 | Carbonaceous |

TABLE 4

Recovery of Model Compounds Using XAD Resins

Percent Recovery from 50 µg/L Samples

| COMPOUND | XAD Resin | | | | | | | | | $CHCl_3$ [b] |
|---|---|---|---|---|---|---|---|---|---|---|
| | 7 | 2/4[a] | 8 | 2/7[a] | 2 | 2/8[a] | 2/4/7/8[a] | 4 | /8[a] | |
| bis-Chloro isopropyl ether | c | 74 | 77 | 76 | 76 | 77 | 71 | 80 | 77 | 92 |
| sym-Tetrachloroethane | 35 | 58 | 59 | 66 | 61 | 68 | 68 | 72 | 72 | 82 |
| n-Hexadecane [d] | 3 | c | c | 8 | 3 | 18 | 14 | c | 11 | 36 |
| alpha-Terpineol | 36 | 76 | 62 | 77 | 81 | 75 | 75 | 80 | 80 | 92 |
| Naphthalene | 64 | 66 | 78 | 77 | 79 | 81 | 82 | 80 | 80 | 87 |
| o-Nitrotoluene | 53 | 75 | 77 | 79 | 82 | 81 | 81 | 83 | 83 | 91 |
| 2-Methyl naphthalene | 63 | 61 | 77 | 72 | 75 | 80 | 81 | 77 | 77 | 86 |
| 1-Methyl naphthalene | 64 | 62 | 80 | 75 | 76 | 82 | 80 | 77 | 79 | 86 |
| Benzothiazole | 40 | 80 | 53 | 75 | 74 | 73 | 77 | 82 | 82 | 96 |
| Phenol | 19 | 30 | 29 | 32 | 14 | 33 | 41 | 38 | 46 | 19 |
| p-Cresol | 33 | 58 | 47 | 50 | 44 | 49 | 60 | 69 | 68 | 50 |
| Acenaphthene | 72 | 68 | 20 | 81 | 99 | 85 | 84 | 81 | 81 | 91 |
| Dibenzofuran | 73 | 70 | 95 | 83 | 93 | 86 | 85 | 82 | 84 | 92 |
| Averages excluding n-Hexadecane [d] | 51 | 65 | 69 | 70 | 71 | 72 | 74 | 75 | 76 | 80 |

a. Mixture of equal dry weights of each resin.

b. Sample directly extracted with two 50-mL portions for comparison with XAD resins.

c. Peak unsuitable for accurate quantitation.

d. Recovery of n-hexadecane low due to extremely low water solubility (see p. 52).

Source: Reference 59

TABLE 5

Comparative Extraction and Elution Efficiency at Different Concentration Levels

| Compound Type | % Recovery - Extraction and Elution | |
|---|---|---|
| | ~50 ppb | ~50 ppm |
| Polyaromatics | 105 | 100 |
| Ketones | 102 | 100 |
| Esters | 100 | 98 |

Source: Reference 28

In the case of partially dissociated compounds, retention is affected strongly by pH changes. Table 6 demonstrates the effect of adding conc. HCl to solutions of organic acids and phenols before passage through an XAD column.

TABLE 6

Comparison of the Recovery Efficiency of XAD-2 for Acids and XAD-4 for Phenols in Distilled Water and Acidified Distilled Water Spiked at the 10- to 50-ppb Level

| ACIDS | % Recovery | | PHENOLS | % Recovery | |
|---|---|---|---|---|---|
| | Untreated | 5 mL HCl | | Untreated | 5 mL HCl |
| Octanoic | 22 | 108 | Phenol | 41 | 40 |
| Decanoic | 8 | 90 | o-Cresol | 62 | 73 |
| Palmitic | 32 | 101 | 3,5-Xylenol | 71 | 79 |
| Oleic | 32 | 100 | o-Chlorophenol | 70 | 96 |
| Benzoic | 7 | 107 | p-Chlorophenol | 75 | 95 |
| | | | 2,4,6-Trichlorophenol | 72 | 99 |
| | | | 1-Naphthol | 43 | 91 |

Source: Reference 28

Addition of $H^+$ to the system converts the acids to their unionized form which show greater affinity for the non-polar XAD-2 resin. The shift in retention of ionizable substances due to pH changes can also be used advantageously in the elution (desorption) stage of the analysis. Table 7 demonstrates the effectiveness of selectively desorbing basic compounds with dilute acid and acid compounds with dilute base.

TABLE 7

Elution of Organic Solutes from a 0.2 g Column of XAD-2 With Aqueous Acid or Base

| Compound | Elution Capability* | |
|---|---|---|
| | 0.05 M NaOH | 1.0 M HCl |
| 2,3,6-Trimethylphenol | ∿25 mL | |
| 3,5-Dimethylphenol | ∿18 mL | |
| 4-Chlorophenol | + | |
| 3,5-Dichlorophenol | ∿15 mL | |
| Phenol | + | - |
| Benzoic acid | + | - |
| Benzenesulfonic acid | + | - |
| 2-Naphthalenesulfonic acid | + | - |
| Dibutyl phthalate | - | - |
| Benzothiazole | - | |
| Acetophenone | - | |
| Pyridine | ∿22 mL | + |
| Indole | - | - |
| Aniline | - | + |
| N-Methylaniline | - | + |
| N,N-Dimethylaniline | - | + |

* + indicates almost immediate elution with eluent solvent front;
- indicates no elution with 25 mL of eluent.

Source: Reference 28

By adjusting the pH of the desorbing solvent, analytes could be separated into two or three fractions before the analytical finish.

Substantial differences exist between results of recovery studies done using natural (river or sea) or tap waters and distilled water. For example, VanRossum and Webb (58) report substantial reductions in percent recovery of some compounds when spiked into local (Athens, Georgia) tapwater at the 50 µg/L level (Table 8). In this experiment, measurements were made to determine the extent of breakthrough and retention on the reservoir wall by chloroform extraction.

TABLE 8

Percent Recovery from 50 µg/L Tapwater Samples

Values in parenthesis are for distilled water.

| Compound | Retained on Reservoir Wall | | Recovered from Resin | | In Aqueous Effluent from Column | |
|---|---|---|---|---|---|---|
| | XAD-2 | XAD-4/8 | XAD-2 | XAD-4/8 | XAD-2 | XAD-4/8 |
| Acenaphthene | 0 | 2 | 79 | 80 | 0 | 0 |
| Acenaphthylene | 0 | 0 | 38(84) | 42(83) | 0 | 0 |
| 2-Benzothiazole | 0 | 0 | 69 | 77 | 26 | 30 |
| Camphor | 0 | 0 | 83 | 87 | 5 | 2 |
| bis(2-chloroethyl)ether | 0 | 0 | 41(110) | 79(94) | 47 | 11 |
| bis(2-chloroisopropyl)ether | 0 | 0 | 85 | 90 | 8 | 0 |
| Di-n-butyl phthalate | 4 | 4 | 91 | 92 | 0 | -- |
| Di-(2-ethylhexyl)phthalate | 22 | 19 | 19 | 26 | 43 | -- |
| p-Dichlorobenzene | 6 | 6 | 71 | 75 | 0 | 0 |
| Dimethyl phthalate | 0 | 0 | 116 | 113 | 0 | -- |
| Fluoranthene | 0 | 0 | 85 | 85 | 0 | -- |
| Hexachlorobenzene | 15 | 11 | 39 | 47 | 28 | -- |
| Hexachlorobutadiene | 27 | 30 | 47 | 49 | 0 | 0 |
| Hexachloroethane | 11 | 12 | 66 | 69 | 0 | 0 |
| n-Hexadecane | 10 | 19 | 16 | 28 | 42 | 31 |
| Naphthalene | 10 | 0 | 84 | 86 | 0 | 0 |
| O-Nitrotoluene | 0 | 0 | 80 | 87 | 0 | 0 |
| Phenol | 0 | 0 | 0(34) | 9(70) | 6 | 0 |
| Pyrene | 5 | 0 | 64 | 68 | 11 | -- |
| a-Terpineol | 0 | 0 | 5(84) | 5(88) | 0 | 0 |
| 1,1,3,3-Tetrachloroacetone | 0 | 0 | 0(22) | 0(53) | 0 | 0 |
| Tri-n-butyl phosphate | 4 | 12 | 85 | 72 | 0 | 0 |
| 2,4,6-Trichlorophenol | 0 | 0 | 20 | 25 | 0 | 0 |
| n-Tridecane | 37 | 43 | 4(5) | 9(6) | 18 | 15 |

Source: Reference 58

The authors attribute the losses in recovery to possible reactions of the analytes with hypochlorous acid and/or other materials in the tapwater. In a study using XAD-2, Osterroht (42) examined the recovery of various non-polar substances from a sea-water matrix at various concentration levels. It was found necessary to include a glass fiber filter to also extract any particulate matter from the sea water as a substantial portion of some of the analytes were evidently adsorbed onto this material. Table 9 presents recovery data of some model compounds from Baltic Sea water at the 1 µg/kg level. (Note: the columns under "sea water pre-extracted" are recoveries from spiked sea water that had previously been passed through the column.)

TABLE 9

Recoveries from Sea Water Spiked with Approximately 1 µg/kg of Substances

| | SEA WATER NOT PRE-EXTRACTED | | | SEA WATER PRE-EXTRACTED | | |
|---|---|---|---|---|---|---|
| | Total % | Fraction | | Total % | Fraction | |
| Substance | Recovery | Particulate | Dissolved | Recovery | Particulate | Dissolved |
| Aldrin | 85 | .72 | .28 | 83 | .54 | .46 |
| Lindane | 24 | | 1.00 | 5 | -- | 1.00 |
| DDE | 89 | .76 | .24 | 84 | .33 | .67 |
| DDT | 96 | .84 | .16 | 102 | .30 | .70 |
| PCB-2 | 86 | -- | 1.00 | 94 | -- | 1.00 |
| Phenanthrene | 57 | -- | 1.00 | 34 | .27 | .73 |
| Pristane | 86 | 1.00 | -- | 48 | .64 | .26 |
| n-Hexadecane | 69 | 1.0 | -- | 44 | .66 | .24 |

Adapted from Reference 42

The author credits the enhanced recovery of the dissolved fraction of the pre-extracted water over the not pre-extracted water to the removal of particulate matter. In the case of the raw sea water, non-polar solutes would tend to adsorb onto the particulate rather than dissolve in the water.

Richard and Fritz (47) used XAD-2 resin to examine the concentration of dieldrin in Skunk River (Ames, Iowa) water over the course of 6 months. A column of 10 mL of resin was used to sample 4L of river

water, and then 200 mL of hot acetonitrile was used to desorb the analytes. Table 10 shows a comparison of this method to solvent extraction of the same river water using 15% hexane in diethyl ether.

TABLE 10

Detected Concentrations of Dieldrin by Two Methods
(parts per trillion)

| Date | XAD-2 | Extraction | Date | XAD-2 | Extraction |
|---|---|---|---|---|---|
| Jan. 8 | 9 | 6 | April 5 | 4 | 4 |
| Jan. 15 | 18 | 13 | April 15 | 14 | 7 |
| Jan. 24 | 4 | 4 | April 22 | 4 | 4 |
| Feb. 1 | 17 | 15 | April 29 | 2 | 1 |
| Feb. 4 | 16 | 16 | May 6 | 5 | 3 |
| Feb. 11 | 20 | 15 | May 13 | 6 | 4 |
| Feb. 19 | 5 | 3 | May 20 | 4 | 3 |
| March 19 | 5 | 2 | May 28 | 9 | 9 |
| March 24 | 8 | 6 | June 3 | 6 | 5 |
| March 30 | 5 | 4 | | | |

Source: Reference 47

The authors also state that these results are the averages of duplicate measurements that generally agree to $\pm 1$ ppt.

Table 11 summarizes some of the other work in the use of macroreticular resins for sampling and analysis of aqueous systems.

Anion exchange resins have quite commonly been employed to adsorb phenols from aqueous media, as a pollution control strategy. However, very little has been done using these resins as a sampling and analysis technique. One exception is the work done by Chriswell and co-workers (10), using Amberlite A-26, a strong anion exchange resin. Table 12 shows recoveries for various phenols added to an Iowa State tap water matrix. In order to prevent premature breakthrough due to other anionic species present, the authors suggested the use of a relatively large (1/2 in x 6 in) column. It is assumed by these researchers, that the species actually adsorbed is the phenolate ion.

TABLE 11

Some Parameters in Recent Use of Macroreticular Resins for Water Sampling

| Resin | Compound Type | Method of Desorption | Solvent | % Recoveries | References |
|---|---|---|---|---|---|
| XAD-2, XAD-7 | Model Compounds | Elution | $(Et)_2O$ | 60-90 | 33 |
| XAD-2, XAD-7 | Model Compounds | Elution | * | 23-100 | 36 |
| XAD-4 | Model Compounds | Thermal | -- | >80 | 37 |
| XAD-4 | Model Compounds | Elution | Acetone | >85 | 34 |
| XAD-2 | Chlorinated Pesticides | Elution | $(Et)_2O$ | ≥89 | 25 |
| XAD-2 | PAH | Soxhlet | $MeCl_2$ | 45-76 | 44 |
| XAD-2, XAD-4 | Trihalomethanes | Elution | $(Et)_2O$ | ≥60 | 29 |
| XAD-4 | Chlorinated Pesticides/PCB | Elution | $(Et)_2O/n\text{-}C_6H_{14}$ | ≥70 | 26 |
| XAD-4 | Trihalomethanes | Elution | (EtOH | -85 | 20 |
| XAD-4, XAD-7 | Phenols | Elution | $Acetone/H_2O$ | NR | 19 |
| IR-45, IRA-93 | | | | | |
| IRA-900 | Phenols | Elution | 4% NaOH | NR | 16 |
| IRA-400's | Phenols | Elution | .5-1.5%, NaOCl | NR | 17 |
| A-26 | Phenols | Elution | $HCl/Acetone/MeCl_2$ | 80-95 | 18 |
| Tenax GC | Chlorinated Pesticides/PCB | Elution | $(Et)_2O$ | ~90 | 20 |
| Tenax GC | Chlorinated Pesticides/PCB | Elution | $(Et)_2O$ | ≥70 | 21 |
| XE-340 | Trihalomethanes | | | NR | 27 |
| XE-348 | Trihalomethanes | | | NR | 28 |

* Elution with $(Et)_2O$ or $CO_3^=$ followed by $OH^-$ followed by MeOH

NR = Not Investigated

TABLE 12

Recovery of Phenols Added to Iowa State University Tap Water

| | Concn. ppb. | Recovery % [a] | Concn. ppb. | Recovery, % [b] |
|---|---|---|---|---|
| Phenol | 500 | 93 | 25 | 95 |
| o-Cresol | 300 | 94 | 25 | 90 |
| p-Cresol | 800 | 96 | 40 | 80 |
| p-Chlorophenol | 900 | 100 | 45 | 95 |
| 4-Chloro-3-methyl-phenol | 800 | 100 | 40 | 95 |
| 2,4,6-Trichloro-phenol | 1100 | 102 | 55 | 95 |
| Pentachlorophenol | 1700 | 89 | 85 | 80 |
| 3,5-Dimethylphenol | 700 | 95 | 35 | 90 |
| 2-Naphthol | 500 | 95 | -- | -- |

[a] Using calibration curve, average of 9 analyses except for 2-naphthol.

[b] Using only a single standard, a single analysis is reported to the closest 5%.

Source: Reference 10

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The Ambersorb XE-340's series resins have become available relatively recently and their use has been confined mostly to work done with trihalomethanes. One study by Mullins et al (38) compared the adsorbent performance of XE-340 resin to 7 brands of activated carbon. This was done by calculations uptake of chloroform at the 10%, 50% and 90% breakthrough points when one inch x 18 inch columns packed with the various sorbents were challenged with a concentration of 50 - 200 µg/L chloroform. The results are given in Table 13. Note that the XE-340 bed did not reach 10% breakthrough indicating high affinity for chloroform.

TABLE 13

$V_{50}$ and Uptake Data for Chloroform on Various Adsorbents

| Carbon Type | Bed Volumes Treated [a] | mg Chloroform Adsorbed cc of Adsorbent |
|---|---|---|
| Filtrasorb 400 | 5,700 | 245 |
| Nuchar WV-G | 4,150 | 135 |
| Nuchar WV-W | 6,000 | 235 |
| Hydrodarco 1030 | 6,400 | 238 |
| Columbia LCK | 6,200 | 269 |
| Witco 950 | 8,000 | 446 |
| Barnebey-Cheney PC-1 | 7,950 | 318 |
| XE-340 | (This resin did not reach 0.10 breakthrough and therefore could not be compared with the other adsorbents studied.) | |

[a] 1 bed volume = 0.232 liters.

Adapted from Reference 38.

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The relative weight capacities for chloroform of various resins was studied by Neely (41). Note that the carbonaceous Ambersorb resins (XE-340's) show very high affinity for this compound (Table 14).

TABLE 14

Chloroform Adsorption by Various Adsorbents

| Adsorbent | Chloroform Capacity (mg/g) at 2 ppm |
|---|---|
| Ambersorb XE-340 | 50 |
| Ambersorb XE-347 | 21 |
| Ambersorb XE-348 | 28 |
| XE-225A | 6 |
| Amberlite XAD-1 | 10 |
| Amberlite XAD-2 | 4 |
| Amberlite XAD-4 | 6 |
| Filtrasorb 300 | 10 |
| Filtrasorb 400 | 12 |
| Nuchar WV-G | 12 |
| BPL (12X30) | 17 |
| Kuhres | 13 |

Adapted from Reference 41. 19

The effect of flow rate on adsorption and, possibly, on overall recovery has been examined by some researchers. It seems intuitively obvious that excessively high flow rates through a packed bed could give rise to a non-equilibrium condition, with respect to the mass transfer of solute between the liquid and sorbent phases. In particular, Stepan and Smith (51) report in creased recovery of some model compounds at the 10 ppm level, for lower flow rates, over a range of 20-200 ml/min. The column used had a 1.2 cm ID, making this a range of ∿20-200 cm/min linear velocity of eluent. Flow rates lower than 20 cm/min were not examined. A similar effect was reported by Chasanov et al ( 9 ), who obtained a factor of 4 increase in the volumetric capacity of IRA-411 (Anion Exchange Resin) for phenol, at a concentration of 3000 ppm, when the flow rate was reduced from 5 to .25 gallons/$ft^3$/min. It is actually the linear or face velocity through the resin bed, rather than the volumetric flow rate of the sample, which limits the efficiencv of mass transfer. However, the linear velocity of the eluent for the Chasanov studies could not be calculated as column dimensions were not specified. Linear velocities of eluent in most other reported studies using macroreticular resins have been on the order of ∿10-50 cm/min.

Stepan and Smith (51) also investigated the effect of flow rate fluctuations on recovery. No difference was noted between the mean of recovery values of large variation vs small variation flow rate runs. However, the precision between runs was poorer when large variations ( $\pm$ 4 mL/min) were allowed.

Resins must be cleaned before use in a sampling environment to ensure sufficiently low blank values. Junk et al (28) reported that sequential Soxlet extraction in 3 solvents (methanol, acetonitrile, diethyl ether) appeared to give the best results. The low temperature and wet environment apparently minimizes disruption of the particles and subsequent exposure of new contaminated inner surfaces. This method was preferred over both vacuum degassing at 225°C and thermal desorption in a 200°C inert gas stream. Evidently, storage of the cleaned resins is also critical. The authors attribute high blank values of napthalene, ethylbenzene and benzoic acid to improper storage. The contaminants are allegedly trapped inside the resin bead during formation and if the resin is allowed to dry out these compounds are released from the interior. Storage under methanol is therefore generally recommended.

D. Other Adsorbents

In addition to macroreticular resins, some research has also been conducted concerning the utilization of other adsorbents for sampling and analysis of organics in aqueous streams. For example, Aue, Kapila and Hastings ( 2 ) report satisfactory recovery of most chlorinated pesticides and PCB using support bonded silicone polymers. A 35 cm x 1 cm ID column was packed with about 7g of 13% $[C_{18}\ H_{37}\ SiO_{3/2}]_n$ on 40-60 mesh Chromosorb G, and used to sample 10L of water spiked with part per trillion levels of chorinated pesticides.

A similar system is marketed by Waters Associates, Inc., Milford, MA, under the trade name SEP-PAK. This is essentially a miniature reversed-phase column, manufactured by bonding $C_{18}$ chains to silica gel. Recoveries of non-polar compounds are quite high. This is consistent with the fact that the driving force behind such a method is the hydrophobic effect. Elution of adsorbed compounds is effected with a solvent such as acetonitrile or methanol.

Phenolic compounds have been isolated from aqueous solution in almost quantitative yield by use of N-vinyl-2-pyrrolidine polymer. Carpenter, Siggla and Carter (8) report recoveries of ≥ 95% using PVP. It is interesting to note that total recoveries are dependent solely upon the efficiency of adsorption, as elution of adsorbed materials was near quantitative using a 4 M area solution (Table 15).

TABLE 15

Recovery of Model Compounds from PVP

| | Initial Conc., ppb | % Removal | % Recovery of Complexed | % Overall Efficiency |
|---|---|---|---|---|
| Phenol | 38.8 | 98. ± 2. | 100 ± 3. | 96. ± 3. |
| p-Cresol | 40.6 | 95. ± 2. | 100 ± 3. | 94 ± 2. |
| Catechol | 40.7 | 97 ± 1. | 99 ± 2. | 95. ± 1. |
| Epinephrine | 37.1 | 92. ± 3. | 101 ± 2. | 92. ± 3. |
| Norepinephrine | 40.0 | 67. (2 trials) | 97.± | 65. |

Source: Reference 8

Finally, there has been some interest in the use of polyurethane as an adsorbent. In particular Gesser and co-workers (20, 21) have detected the presence of PCB and other organics from laboratory and river water using polyurethane foam plugs. They estimate that analyte levels were in the 5-10 parts per trillion range. Foam plugs (8.3 cm ID x 5 cm) were packed into a glass adsorption column and ~1500 L of river or treated municipal drinking water were passed through at a rate of 5 to 10 L/hour. However, extraction efficiencies of polyurethane foam were shown to be, in general, poorer than either solvent extraction or extraction by XAD resins (59).

Another type of urethane, open-pore polyurethane (OPP), was used for the analysis of polynuclear aromatic hycrocarbons in water. Navratil, Sievers and Walton, (40) examined the extraction efficiency, elution efficiency and flow rate dependence of laboratory prepared OPP, using pyrene as the analyte. They report excellent recoveries (Table 16) of several PAH.

TABLE 16

Recovery of PAH with OPP

| PAH | Flow Rate L/h | PAH Loaded µg | Recovery % |
|---|---|---|---|
| Benzo(a)pyrene | 1.8 | 4 | 95 ± 6 |
| Biphenyl | 0.9-1.5 | 5-6 | 98 ± 5 |
| Fluoranthene | 0.5-1.0 | 4-5 | 77 ± 4 |
| | 0.5-1.0 | 1-2.5 | 97 ± 3 |
| Naphthalene[a] | 0.1 | 5 | 56 ± 3 |
| | 0.1-1.0 | 1-2.5 | 98 ± 10 |
| Phenanthrene | 0.8-1.0 | 5 | 58 ± 7 |
| | 0.8-1.0 | 1-2.5 | 92 ± 9 |
| Pyrene | 0.6-0.8 | 1-1 | 100 ± 2 |
| | 1.2-1.7 | 4-5 | 89 ± 3 |
| Pyrene (XAD-2)[a] | 0.6 | 4 | 79 ± 8 |

[a] Required 10 mL of methanol to elute quantitatively; others needed only 5 mL.

Source: Reference 40

## IV. EXPERIMENTAL

### A. Approach

The experimental work involved a systematic study of a wide range of macroreticular resins, to determine their usefulness for general and compound-specific sampling of organics from aqueous systems. Since the sampling and analysis procedure entails two processes, adsorption and desorption, separate studies were made of each process. The adsorption process was examined by the use of breakthrough curves, while the desorption process was examined by recovery experiments. The effects of flow rate, concentration and method of desorption were studied in this work.

#### 1. The $V_{50}$ Approach

When a solution containing an analyte is passed through an adsorption column, the analyte is adsorbed by the sorbent and the solvent passes through the column unaffected. However, the capacity of the adsorbent for the analyte is finite. Eventually the solute will begin to emerge from, or break through, the column.

It is important to distinguish between two possible types of capacity limitations. Exceeding the intrinsic weight capacity of a sorbent, by saturating all of the available adsorption sites, can occur at very high analyte loadings. It is this phenomenon which leads to the high concentration plateau behavior of the familiar Langmuir isotherm. However, in most sampling situations it is volumetric capacity of the sorbent, not weight capacity, which governs the breakthrough characteristics. The volumetric capacity limit results from partitioning of the analyte between a stationary phase, the adsorbent, and a mobile phase, the sample matrix, exactly as in a chromatographic process. Analyte adsorbed at the head of the column at time zero will be swept out the back of the column after a sufficient volume of aqueous phase has passed through. This process causes breakthrough to occur at column loadings well below the inherent weight capacity limitation. Volumetric capacity is limiting at analyte concentrations of about 100 ppm (w/v) and below. It is especially important to recognize that when volumetric capacity is limiting, then breakthrough is independent of concentration. Thus a 10 ppb solution will break through the column just as rapidly as a 10 ppm (10,000 ppb) solution of the same analyte.

Study of the breakthrough phenomenon under conditions where volumetric capacity is limiting is an especially useful way of characterizing sorbent/analyte systems for sampling applications. A breakthrough curve is generated, by monitoring the concentration of the solute in the effluent as a function of time. A typical experimental breakthrough curve is shown in Figure 1. The vertical axis shows concentration of analyte in the effluent (in this case measured by UV adsorbance) and the horizontal axis indicates time, in cm of chart paper. Rather than using the units of concentration vs. time, breakthrough curves are usually normalized. The concentration is expressed as percent breakthrough $C/C_0$, where C is the measured concentration of analyte in the

column effluent and $C_0$ is the feed concentration, while the horizontal axis displays volume, in mL or bed volumes (mL/cc resin), passed through the column.

Of particular interest in characterizing a specific system is the value of $V_{50}$, that is, the volume of solution (mL) necessary to give 50% breakthrough for a given bed volume (cc) of sorbent. Figure 2 shows the location of the $V_{50}$ point and its relationship to several other points on the breakthrough curve. Note that due to the shape of the breakthrough curve the value of 1/2 $V_{50}$ is not necessarily the same as the value of $V_{25}$. In fact, the breakthrough at 1/2 $V_{50}$ is significantly lower than 25%, as long as an equilibrium system is maintained. A measure of $V_{50}$ is necessary and sufficient to characterize a solute/sorbent pair provided that the sorbent is not so overloaded that weight capacity effects are important (Appendix A). A high $V_{50}$ represents a high degree of retention, whereas a low $V_{50}$ is representative of a low degree of retention. For the purposes of extracting compounds from solutions, a high $V_{50}$ is, therefore, desirable. Measurements of $V_{50}$ were used in optimizing the choice of adsorbents for this task.

2. Uptake and Uptake Efficiency

In conjunction with the measurement of $V_{50}$, another useful characteristic of the system is obtainable from the breakthrough curve. Since the breakthrough curve is a representation of instantaneous effluent concentration versus sample volume, the area under the curve is proportional to the mass of solute that has broken through the column. Therefore, the area above the curve is proportional to the mass of solute adsorbed by the substrate. Figure 3 demonstrates this point graphically.

Collection or uptake efficiency, E, is defined as the ratio of mass of solute taken up to the total mass of solute introduced into the column. High uptake efficiency is desirable in designing a sampling system so as not to loose a large portion of the analyte due to breakthrough. One of the criteria in designing the full-scale system was the collection efficiency of the adsorbents in question.

3. Recovery

Although uptake is important, it is only one-half of the sampling and analysis procedure. Recovery of adsorbed analytes from the resin is also a significant step. The method of desorption was therefore examined in the study. The product of uptake efficiency and desorption efficiency gives the overall percentage recovery of the organic analyte from water.

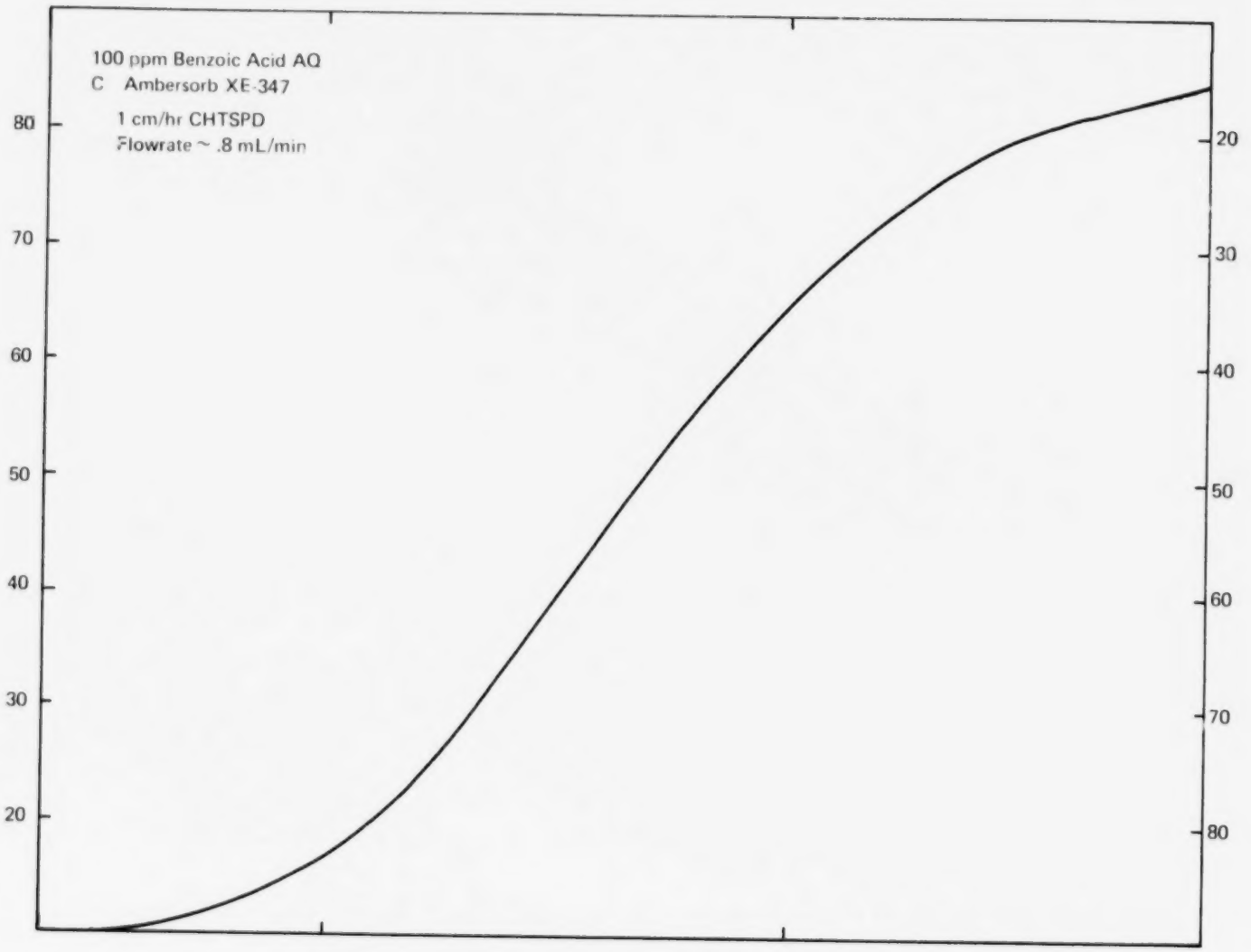


FIGURE 1 TYPICAL EXPERIMENTAL BREAKTHROUGH CURVE

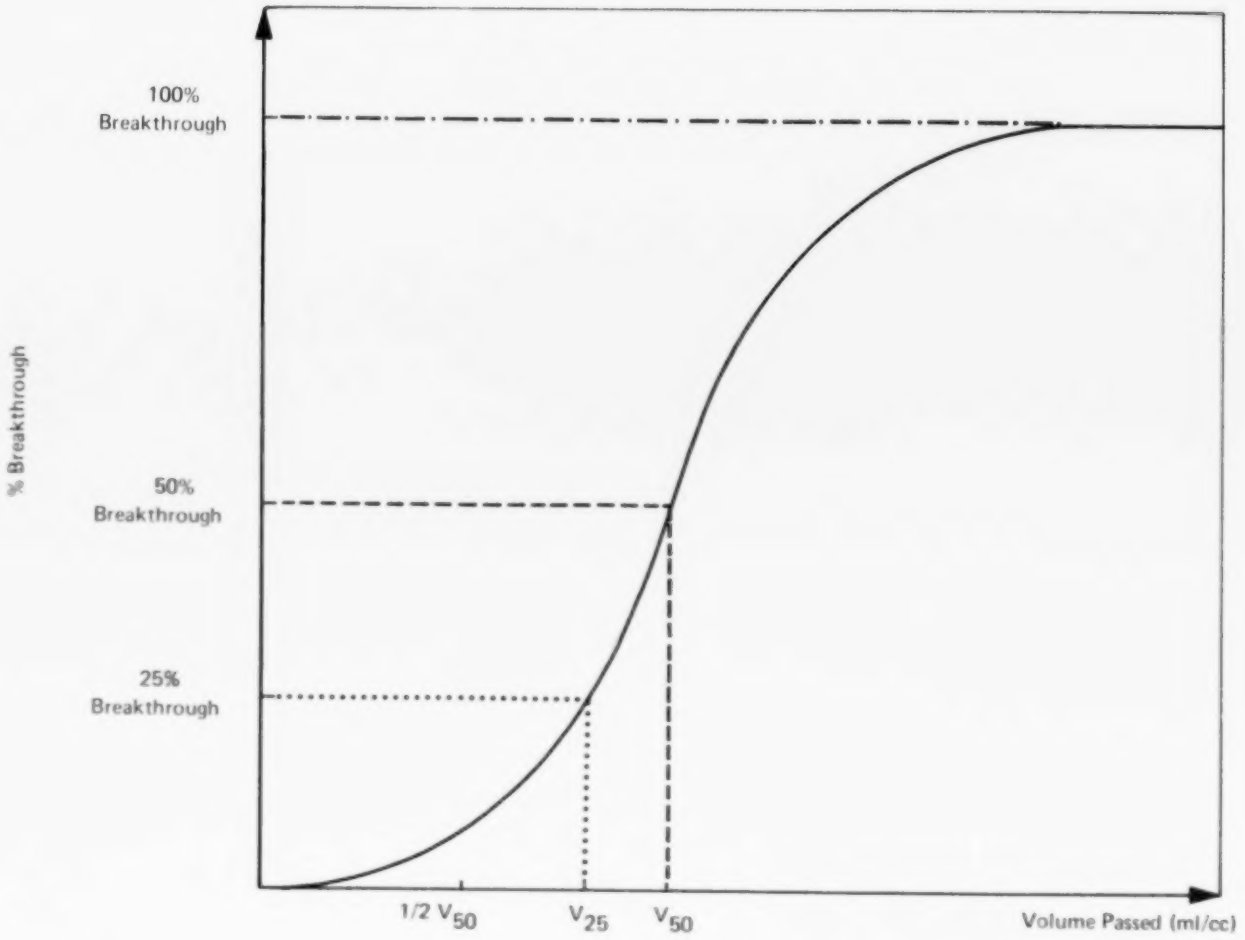


**FIGURE 2 SOME MEASUREMENTS ON A BREAKTHROUGH CURVE**

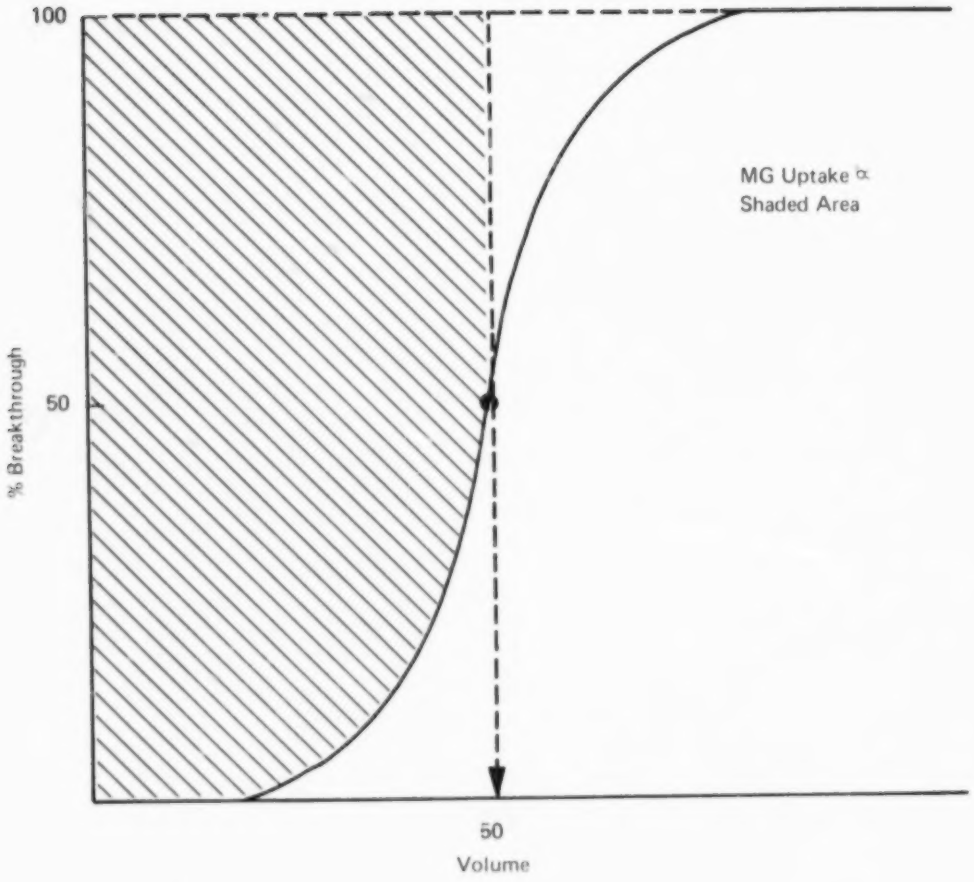


**FIGURE 3 UPTAKE OF SOLUTE AS DEPICTED BY BREAKTHROUGH CURVE**

## B. Experimental Details

### 1. Laboratory Scale Experiments

The apparatus used to generate breakthrough curves is shown, in block diagram form, in Figure 4. The actual apparatus is shown in Figure 5. Solutions of specific analytes are pumped using a positive displacement pump to a 3-way rotary valve. This valve enables the flow of sample to be directed to the detector, by way of a bypass loop, or to the adsorption column and then the detector. All solutes used in this study were selected to have considerable UV adsorbance at 254 nm, allowing the use of a UV detector to monitor the effluent concentration. The output of the detector was plotted on a strip chart recorder.

The procedure for generating a breakthrough curve was as follows: the system was assembed and flushed with methanol, followed by distilled, deionized, degassed water. The test column was packed with the appropriate resin and distilled, deionized, degassed water was pumped through (with the rotary valve set to "column") until a stable baseline was obtained. This was 0% breakthrough. The flow rate was checked at the detector outlet with a 2.0 mL pipette and a stopwatch. The valve was then switched to "bypass" and the sample, prepared in distilled, deionized, degassed water was pumped through the system. The detector response at this point was taken to be 100% breakthrough. Sample flow was then switched back to the column, and the breakthrough curve recorded.

Generation of loaded resin columns for recovery experiments was done in a similar manner, except that a total sample volume was chosen, based on previously obtained breakthrough data, that would not produce any solute breakthrough. Desorption of the solute from the resin was done by 24-hour Soxhlet extraction with methylene chloride for non-polar solutes and methanol for some polar solutes. Quantification of all recovered solutes, except phenol, was done by gas chromatography. Phenol recoveries were quantified by using an aminoantipyrene colorimetric procedure.

### 2. Full Scale Experiments

The experimental apparatus used in the full scale experiments is shown in block diagram form in Figure 6.

The system was flushed with methanol, then distilled, deionized water. A 10 L sample was then passed through the cartridge at a flowrate of 42 mL/min (10 L in 4 hours). During the run, samples of the effluent were taken at intervals. These samples were subsequently analyzed to check for breakthrough by determining UV absorbance at 254 mn.

The cartridge was loaded in a manner that kept two sequential resin beds separate, so that the extraction and analytes of the adsorbed compounds could be made separately. The contents of each half of the cartridge were placed in separate Pyrex Soxhlet thimbles which had been previously

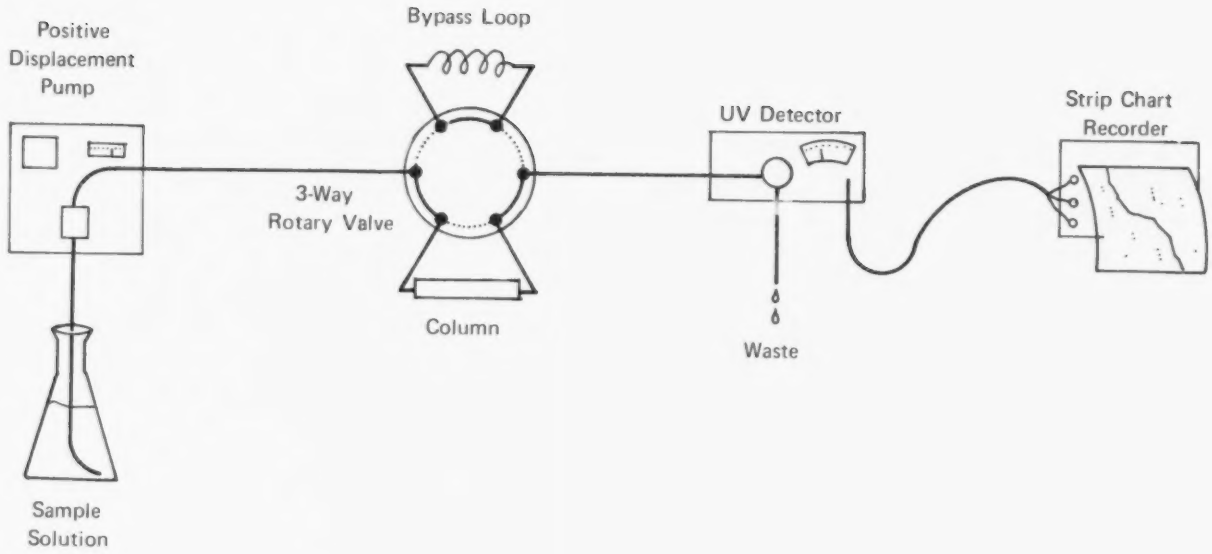


FIGURE 4 BLOCK DIAGRAM OF EXPERIMENTAL SET-UP FOR GENERATION OF BREAKTHROUGH CURVES

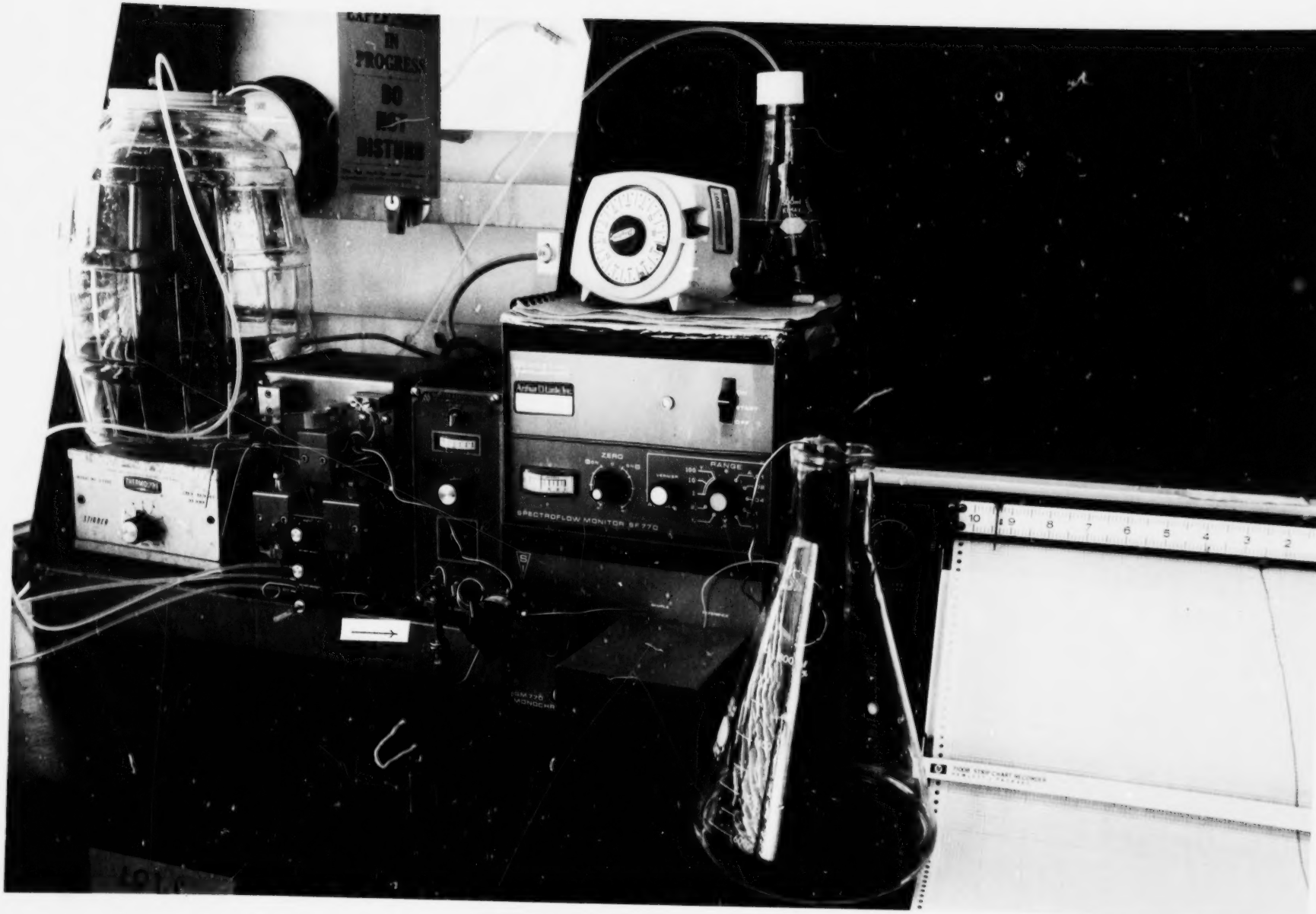


FIGURE 5. Experimental Set-up for Generation of Breakthrough Curves. Arrow Points to Laboratory Scale Sorbent Cartridge.

FIGURE 5 EXPERIMENTAL SET-UP FOR GENERATION OF BREAKTHROUGH CURVES. ARROW POINTS TO LABORATORY SCALE SORBENT CARTRIDGE

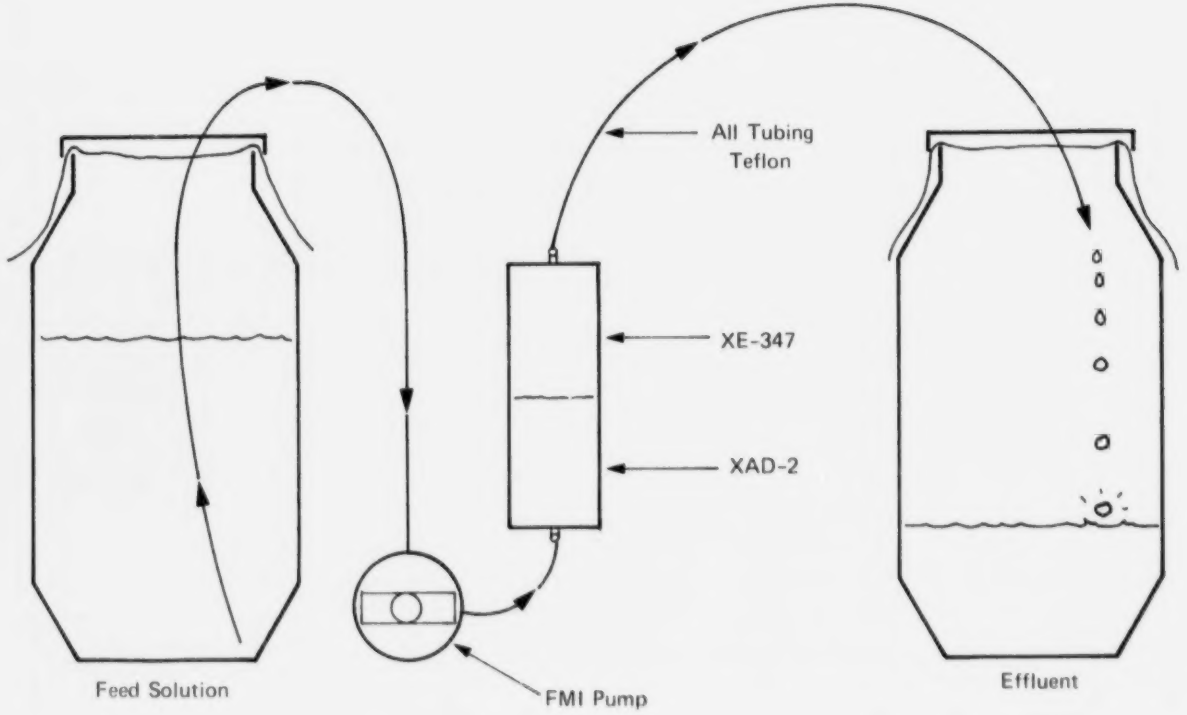


**FIGURE 6 BLOCK DIAGRAM OF FULL SCALE EXPERIMENTAL SET-UP**

extracted. To remove as much water as possible, these thimbles were attached to suction flasks and aspiration vacuum was applied, drawing most of the water through. After 12 minutes of air-drying, the thimbles were placed in Soxhlet extractors. Because of the possibility of losses or contamination during air-drying, this procedure is not recommended for general use. It is not necessary to air-dry prior to the *in situ* extraction procedure (below), which is recommended.

The solvent for extracting the XAD-2 resin was methylene chloride, whereas the solvent used initially for the XE-347 resin was methanol. On later runs it was determined that methylene chloride was acceptable for extracting both resins.

The last full-scale experiments, which included analysis of a sample of aqueous effluent from a coking operation, were extracted *in situ* with methylene chloride by use of a continuous extractor (Figure 7).

3. Preparation of Resins

All resins were purchased from Rohn and Haas Co., Philadelphia, PA. Resins were cleaned in batches of approximately 500-800 g. To remove fines and preservatives, the resins were first washed with tap water. The remaining material was transferred to a giant Soxhlet apparatus (23 cm x 8.5 cm I.D., thimble) and consecutively extracted with 3 solvents: distilled, deionized water (8 hours), methanol (24 hours) and methylene chloride (24 hours). After extraction, the resins were removed from the Soxhlet apparatus and stored in acid-washed, amber glass bottles under methanol.

4. Preparation of Adsorption Column

Laboratory scale columns were made from 0.5 cm I.D., stainless steel tubing, either 3.0 or 6.2 cm in length. Reeve Angel 2 μm pore size stainless steel frits were placed at either end to minimize the effects of particulate materials and to provide a flat, consistent bed. Columns were packed with a methanol slurry of the resin, with intermittent applications of vibrations from a vibro-engraver to ensure a reproducible packing. The end caps were Swaglock 6.4 mm to 1.6 mm reducing unions.

The full-scale sampling cartridge was stainless steel 3.8 cm I.D. tubing. Plans for the full-scale cartridge appear in Figure 12. Packing the trap with the resin beads was found easiest when vacuum was applied to the bottom (by aspirator). The cleaned resin beads were loaded with a metal spoon and packed by drawing water through the bed. The XAD-2 resin was first loaded into the bottom stage; then the separating ring was dropped in, followed by the XE-347 resin. Finally the top was screwed on and both end caps tightened.

5. Solutions

Solutions of analytes for laboratory-scale experiments were made with reagent grade solutes in MilliQ water. Solutions for full-scale experiments were made by spiking 10 L of MilliQ water with 10 mL of a 10 g/L concentrated solution of the analytes in methanol.

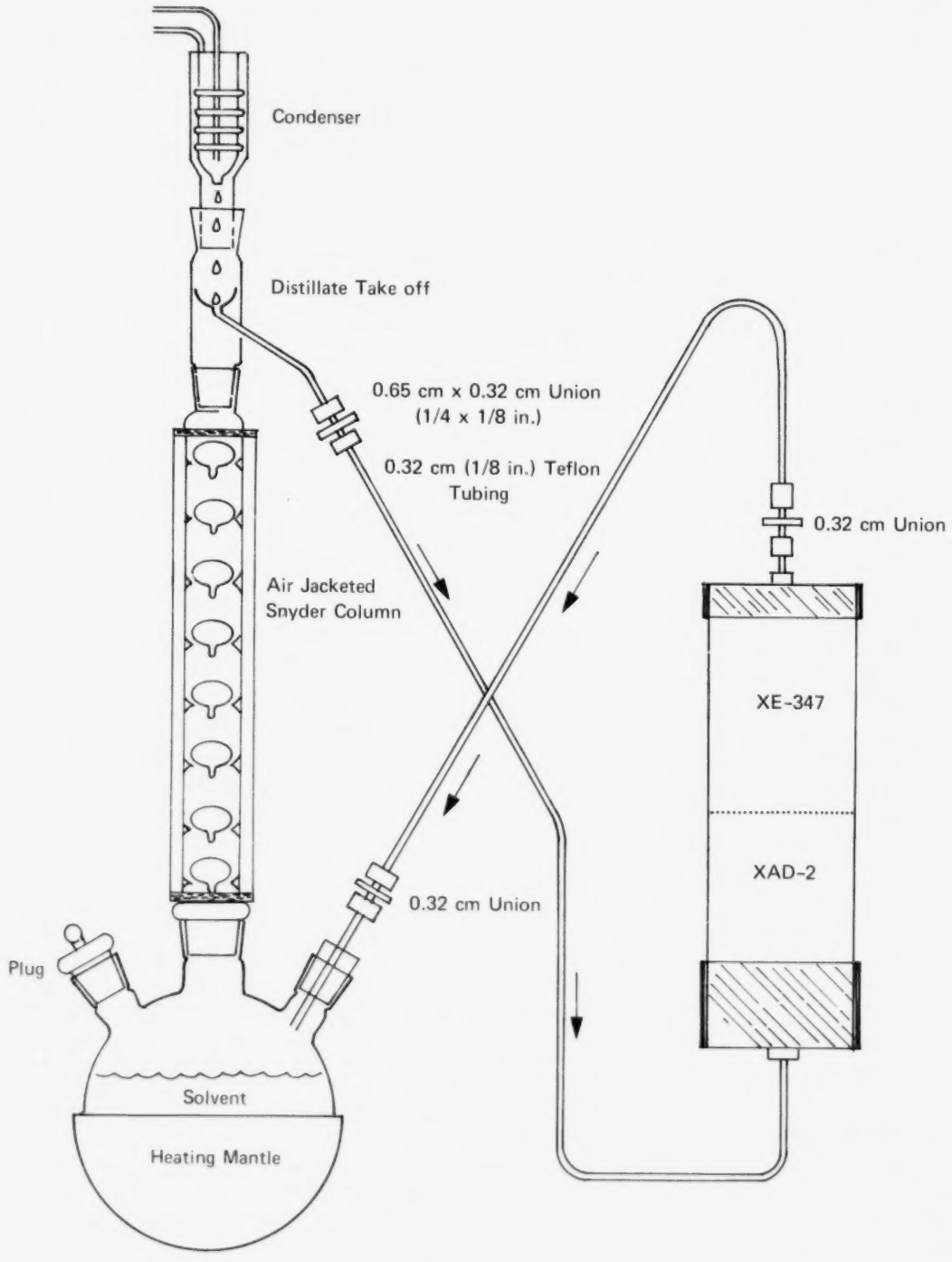


**FIGURE 7 BLOCK DIAGRAM OF CONTINUOUS EXTRACTION APPARATUS**

## 6. Equipment

Solutions were passed through the laboratory-scale column by means of a liquid chromatography pump (Waters M6000A, LDC ConstaMetric III or Milton Roy 396). A Fluid Metering Inc., lab pump was used to deliver the sample to the full-scale cartridge.

All connections were made with 1.6 mm stainless steel tubing or 1.6 mm Teflon tubing (3.2 mm for full-scale cartridge), using Swaglock fittings. The Bypass/Column valve was either a Cheminert Model R6031V4 (LDC) or a Chromtronix HP-SV.

Detection of breakthrough in the laboratory-scale experiments was by UV absorbance at 254 nm. The detectors used were: Waters 440, Schoeffel SF-770, LDC 1205 UV Monitor or LDC 1220 UV DuoMonitor. Output of the detector was directed to either a Hewlett Packard or a Linear strip chart recorder.

Two gas chromatographs were used in this work. Recovery of compounds sorbed in laboratory-scale experiments was quantified on a Varian model 2740 gas chromatograph equipped with a flame ionization detector. The column used was a Supelco 10% OV-101, 1.83 m x 3.2 mm stainless column. Peak areas were integrated using a SpectraPhysics Autolab System I Integrator.

Full-scale cartridge recoveries were quantified on a Hewlett Packard 5840A gas chromatograph, using the same column, and a flame ionization detector. Chromatographic conditions were:

Initial Temperature: 45°C
Isothermally for 5 minutes, then 10°C/min. to 260°C
Injector Temperature: 275°C
Detector: Flame Ionization @ 350°C
Flow Rate of He gas: 20 mL/min

## V. RESULTS AND DISCUSSION

### A. The Effect of Flow Rate (Linear Velocity)

One important consideration in the design and utilization of a sorbent cartridge is the rate at which the sample passes through the column. The advantage of using a high flow rate is that the sampling time, for a given volume of sample, is reduced. High flow rate, however, may have significant disadvantages. A higher flow rate usually produces a higher pressure drop across the column. (This sometimes requires the use of high pressure tubing, such as steel, instead of Teflon.) More importantly, though, high flow rate affects retention.

Flow rate is usually expressed in terms of volume of solution per unit time (e.g., mL/min). The critical parameter, however, is not flow rate per se, but rather the linear velocity of the solution through the column. This is because a measurement of linear velocity takes into account the diameter of the column and thus the mechanics of mass transfer, while a measurement of flow rate does not. Using linear velocity, conclusions drawn from observations of a small scale system can be extrapolated, or scaled up, to a larger scale system.

The effects of linear velocity on adsorption were studied by generating breakthrough curves at various linear velocities. Figure 8 shows breakthrough curves, up to the 50% breakthrough point, for a particular system at six different linear velocities. Apparent linear velocity (face velocity) was calculated as:

$$L = F/\pi r^2$$

where F is the flow rate (mL/min) and r is the radius of the column (cm).

At low linear velocities (e.g., 4.0 cm/min) the breakthrough curve is virtually independent of this parameter. This is especially evident in that the value of $V_{50}$ is unchanged with respect to flow rate, and is consistent with the fact that, in elution chromatography, the retention volume of a specific compound is also independent of flow rate (at low flow rates).

As the linear velocity is increased, the breakthrough curve begins to shift closer to the vertical axis. This means that the solute begins to break through sooner. The effect of linear velocity on $V_{50}$ is shown in Figure 9. Note again that at low flow rates $V_{50}$ is independent of flow rate, but at higher flow rates the value of $V_{50}$ begins to decrease. For example at 4.0 cm/min, $V_{50}$ for acetophenone on XAD-2 is 650 mL/cc resin, whereas at 20 cm/min the value for $V_{50}$ is 350 mL/cc. It is important to note, that it is not safe to assume that doubling the flow rate will halve the breakthrough time. For instance, at 5 cm/min $V_{50}$ occurs at $\sim$12 hours while at 10.0 cm/min $V_{50}$ occurs at $\sim$5 hours, and at 20 mL/min $V_{50}$ occurs at $\sim$1.8 hours.

Another effect, which had not been specifically expected, is the effect of linear velocity on the shape of the breakthrough curve.

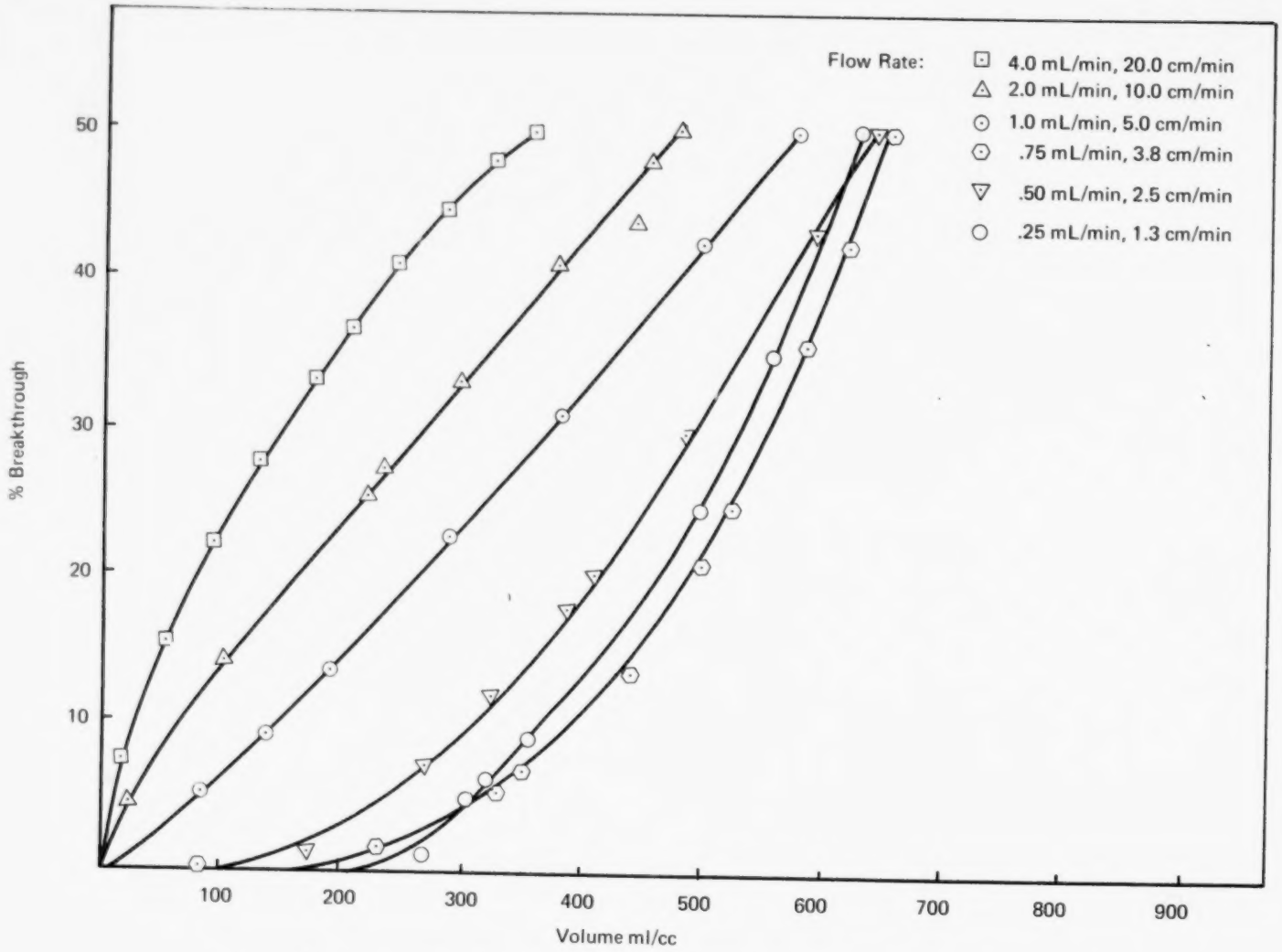


FIGURE 8 NORMALIZED BR AKTHROUGH CURVES AT VARIOUS FLOW RATES (10 ppm ACETOPHENONE ON XAD-2 6.2 cm x 0.5 cm I.D. COLUMN)

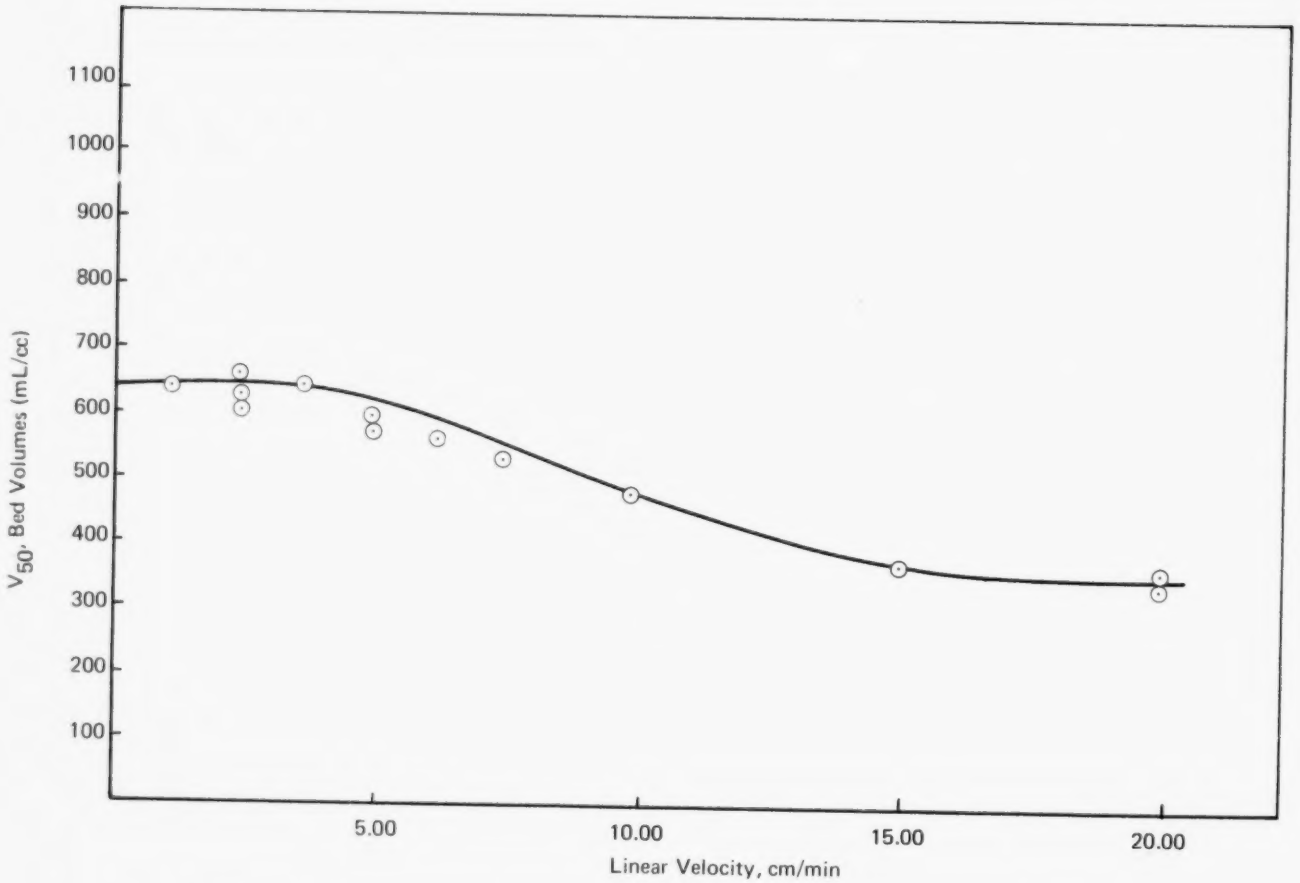


FIGURE 9 $V_{50}$ AS A FUNCTION OF FLOW RATE (10 ppm ACETOPHENONE ON XAD-2 6.2 cm x 0.5 I.D. COLUMN)

Figure 8 illustrates that at low linear velocities, the breakthrough curve has a distinctive concave appearance, while as the linear velocity is increased, the curve becomes distorted. Since uptake is proportional to the area above the curve, one can see that uptake efficiency is greater than the curve is concave than when it is convex. The effect of linear velocity on uptake efficiency is depicted in Figure 10. Uptake efficiency was measured at two points, The $V_{50}$ point and 1/2 $V_{50}$ on a series of experimental breakthrough curves like those in Figure 8. Note that as linear velocity increases, efficiency decreases. Collection efficiency at the 1/2 $V_{50}$ point is almost 100% at low linear velocities but considerably lower at high linear velocities.

The combination of these two effects can be illustrated by an example:

Assume that one wished to sample 400 mL of a 10 ppm solution of acetophenone using a .5 cm ID x 6.2 cm column of XAD-2. Also assume that 400 mL were passed through two columns, one at 4.0 cm/min and the other at 10.0 cm/min. In each case, the volume of sample passed would be 325 mL per cc of resin bed.

The first column would sample this volume of solution at 4 cm/min in

$$400 \text{ mL} \times \frac{1}{.1963 \text{ cm}^2} \times \frac{1}{4.0 \text{ cm/min}} \times \frac{1 \text{ hr.}}{60 \text{ min}} = 8.5 \text{ hours}$$

The second column would sample this volume of solution in

$$400 \text{ mL} \times \frac{1}{.1963 \text{ cm}^2} \times \frac{1}{10.0 \text{ cm/min}} \times \frac{1 \text{ hr.}}{60 \text{ min}} = 3.4 \text{ hours}$$

The more rapid sample flow rate is clearly more convenient from the point of view of sampling time constraints. However, the collection efficiencies would be very different for the two sampling scenarios. Integrating the area above the breakthrough curve (Figure 8) for the 4.0 cm/min case indicates a 97.5% collection efficiency. A similar integration shows that a collection efficiency of only 82.5% would be achievable for the 10 cm/min flow rate. Thus decreased collection efficiency would be significant despite the fact that the sampled volume in each case corresponds to only one-half of the calculated $V_{50}$ value for this sampling system. This illustrates that flow rate can affect not only the 50% breakthrough point but also the initial collection efficiency. These flow rate effects are most probably due to the fact that higher flow rates hinder mass transfer between phases in the column. The net effect of this kinetic non-equilibrium is a decrease in the effective capacity of the column.

In order to assure proper mass transfer of solute, the linear velocity was set at approximately 4.0 cm/min in subsequent breakthrough experiments with other analytes and sorbents.

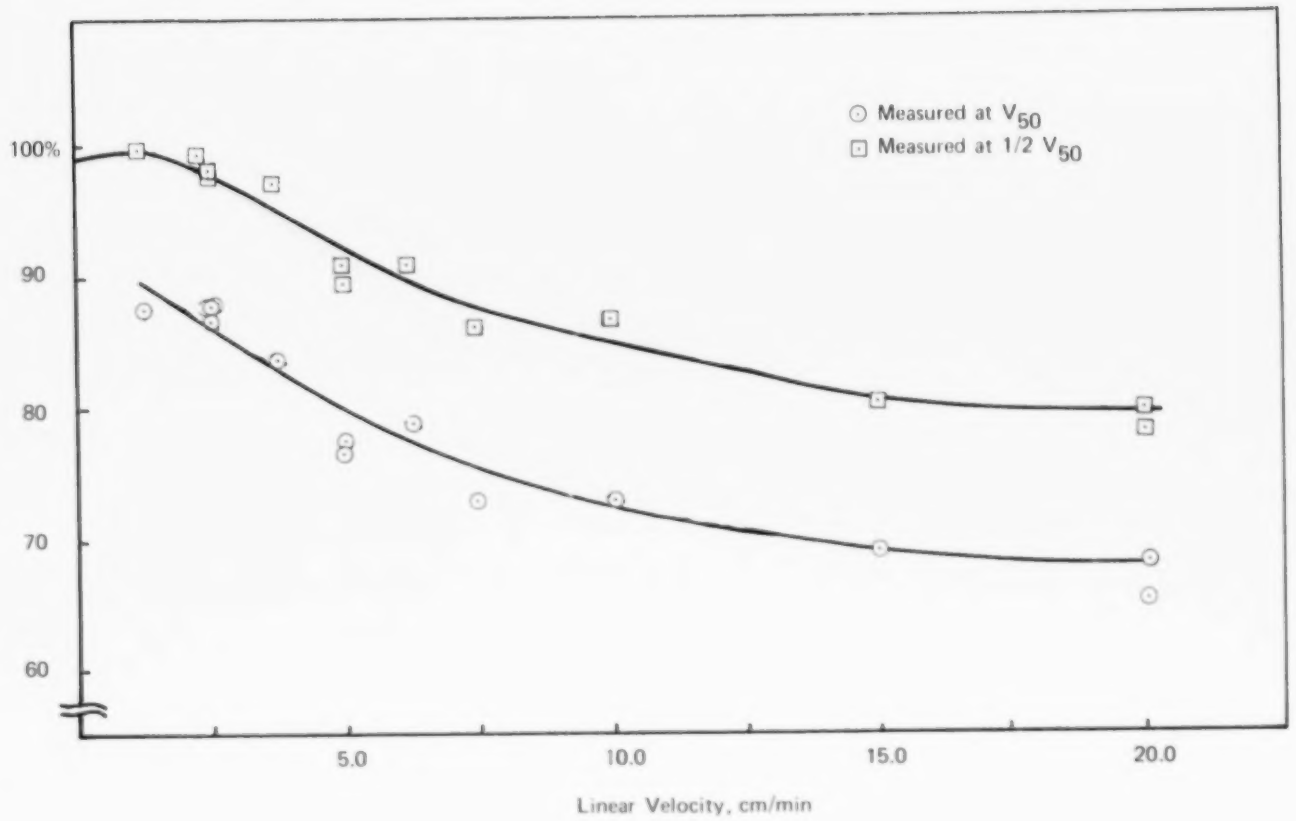


**FIGURE 10 COLLECTION EFFICIENCY AT VARIOUS LINEAR VELOCITIES**
**(10 ppm Acetophenone on XAD-2, 6.2 cm x 0.5 I.D. Column)**

These pronounced mass transfer effects on adsorption at relatively low flow rates had not been expected based on results previously published. For example, Strup et.al., (52) had reported good recoveries of PAH using XAD-2 at water flow rates corresponding to ∿60 cm/min linear velocity. One hypothesis that reconciles these disparate observations is that adsorption of species for which XAD-2 has limited affinity, such as acetophenone, is limited by diffusion into the pores of the macroreticular resin particles, while more readibly sorbed species such as PAH, are efficiently captured on the exterior surface of the particles.

Support for this hypothesis is provided by reports (2,3,12) that PAH can be sampled using relatively low surface area sorbents (3, 4, 40) such as foam plugs. Also, the present work has shown that very poorly sorbed species, such as phenol, show mass transfer effects even at the lowest velocities tested. The flow rate dependence study illustrates the fact that sampling approaches proved effective for PAH in water are often not directly applicable to other organics.

It should be noted that once an appropriate linear velocity criterion has been determined for a sorbent/analyte combination in a chromatographic experiment, it can be used in design of a large-scale sampling system. For example, assuming a 4.0 cm/min velocity criterion and a 4-hour, 10-liter water sampling constraint, one can calculate that a sorbent cartridge of at least 3.7 cm diameter would be required.

## B. Sorbent/Solute Interactions

A systematic study was performed to determine the retention behavior of several sorbents when challenged with specific model organic compounds as solutes. Table 17 shows the different macroreticular resins used in this study and presents some data on the physical characteristics. For more detail, see Appendix B, "Macroreticular Resins."

TABLE 17

Physical Properties of Macroreticular Resins Examined

| Resin | Chemical Type | Surface Area $m^3/g$ |
|---|---|---|
| XAD-2 | Styrene-Divinylbenzene | 330 |
| XAD-7 | Acrylic Ester | 450 |
| XE-340 | Carbonaceous | 400 |
| XE-347 | Carbonaceous | 350 |
| XE-348 | Carbonaceous | 500 |
| IRA-904 | Styrene-Divinylbenzene Strong Anion Exchange | NA |
| IRA-93 | Styrene-Divinylbenzene Weak Anion Exchange | NA |

The model compounds included both non-polar and highly polar organics.

### 1. Non-Polar Compounds

From an extensive review of the literature it was deduced that XAD-2 resin was a satisfactory sorbent for sampling of non-polar compounds. To confirm this, XAD-2 was examined in initial studies. Table 18 presents $V_{50}$ data obtained for non-polar model compounds on XAD-2 resins.

It is apparent from these data that this resin has a high affinity for non-polar compounds, as was observed by other workers (59, 42, 52). Note that in the case of napthalene and chlorobenzene no breakthrough at all was observed after 400 mL/cc had been passed.

Recovery studies were also performed to ensure that XAD-2, an excellent adsorbent, would also provide satisfactory desorption characteristics. Table 18 also contains recovery data for two compounds.

In light of these two studies, it was concluded that XAD-2 was indeed a suitable sorbent for sampling and analysis of non-polar organic compounds.

TABLE 18

$V_{50}$ and Recovery Data for Non-polar Compounds on XAD-2 Resin [a]

| Compound | $V_{50}$, mL/cc | % Recovery |
|---|---|---|
| Acetophenone | 650 | 88.9 |
| Methyl benzoate | 1790 | -- [c] |
| Naphthalene | -- [b] | 99 |
| Chlorobenzene | -- [b] | -- [c] |

[a] Concentration: 10 mg/L
Column: 5 cm ID x 6.2 cm
Flow Rate: .88 - .92 mL/min

[b] No breakthrough after 400 mL/cc was observed

[c] Not determined

2. Polar Compounds

Due to the demonstrated success of XAD-2 resin for collection of non-polar compounds, this resin was evaluated using polar compounds as well. Table 19 shows $V_{50}$ data for some polar compounds on XAD-2. These data demonstrate that XAD-2 has a significantly lower affinity for polar compounds than non-polar compounds. Affinity for phenol is so low that in order to sample a 10 L sample with 97% collection efficiency (i.e., at 1/2 $V_{50}$) a resin bed of 267 cc would be necessary.

TABLE 19

$V_{50}$ Data for Polar Compounds on XAD-2 and XAD-7 [a]

| Compound | $V_{50}$, mL/cc | |
|---|---|---|
| | XAD-2 | XAD-7 |
| Phenol | 75 | 115 |
| Benzoic Acid | 101 | 84 |
| Benzyl Alcohol | 99 | -- [b] |

[a] Concentration: 10 mg/L
Column: .5 cm ID x 3.0 cm
Flow Rate: .88 - .92 mL/min

[b] Not determined

Table 19 also shows $V_{50}$ data for the polar model compounds on XAD-7, a more polar, acrylic ester resin that has previously been used for collection of these species. However, these $V_{50}$ values are within the same range as the XAD-2 values. This indicates that neither XAD-2 nor XAD-7 is really satisfactory for the sampling of polar species. It is interesting to note that XAD-7 was found to have a higher affinity for phenol, but lower affinity for benzoic acid than XAD-2. A similar result had been reported by Thurman, et al., (57), who interpreted their results in terms of specific $\pi$-$\pi$ interactions between benzoic acid and XAD-2 not possible with the polyacrylic XAD-7.

In contrast to XAD-7, the carbonaceous resins, XE-340, XE-347 and XE-348 showed high affinity for the polar compounds tested. At 10 mg/L phenol, for example, no breakthrough occurred after 16 hours (1600 mL/cc). It was decided, therefore, to increase the challenge concentration to 100 mg/L, in order to obtain measurable breakthrough in the studies, these XE series resins. At this challenge concentration, premature breakthrough occurred because sorbent weight capacity limitations began to override volumetric capacity limits. Although the breakthrough curve thus generated corresponded to non-equilibrium conditions and was therefore much less useful for design of sampling systems, valid comparative data for several sorbent solute pairs can be generated under these conditions.

Comparisons among the XE-340 series resins were made using benzyl alcohol as the analyte. Table 20 presents $V_{50}$ data for some polar compounds on the Ambersorb resins. XE-347 had slightly greater affinity for benzyl alcohol than XE-348, and significantly greater affinity than XE-340.

TABLE 20

$V_{50}$ Data for Polar Compounds on Carbonaceous Ambersorb Resins [a]

| Compound | $V_{50}$, mL/cc | | |
|---|---|---|---|
| | XE-347 | XE-348 | XE-340 |
| Phenol | 584 | --[b] | --[b] |
| Benzoic Acid | 870 | --[b] | --[b] |
| Benzyl Alcohol | 623 | 582 | 161 |

[a] Concentration: 100 mg/L (see text)
Column: .5 cm ID x 310 cm
Flow Rate: .88 - .95 mL/min

[b] Not determined

The $V_{50}$ values for polar analytes on XE series resins are at least 5-10 times higher (allowing for differences in challenge concentration) than those for the XAD series. One possible explanation of the higher affinity of the Ambersorb resins is their higher specific surface area; however, this can account for no more than a factor of two difference in $V_{50}$ (700 $m^2/g$ for XE-347 vs. 330 $m^2/g$ for XAD-2). Therefore, the large increase in $V_{50}$'s for XE-347 compared to XAD-2 must reflect stronger specific interactions with the more active carbonaceous surface of the XE-347. The specific retention mechanism is not known, but the XE series resins are moderately polar, therefore, implicating fairly strong dipole-dipple interactions in the adsorption process.

Recovery studies using the XE-347 resin are shown in Table 21. Recoveries of similar compounds are generally somewhat lower from this resin than XAD-2 resin. A possible explanation is the carbonaceous surface, which may, like carbon, show extremely strong solute-sorbent bonding.

TABLE 21

Recovery Data for Polar Compounds on XE-347 Resin

| Compound | % Recovery |
|---|---|
| Phenol | 46.8 |
| Acetophenone | 78.6 |
| Diethylphthalate | 93.3 |

### 3. Ion Exchange Resins

The ion exchange resins initially showed promise for polar organics, with IRA-93 and IRA-904 showing substantially higher capacity for phenol and benzoic acid in distilled, deionized water than did XAD-2 or XAD-7 (Table 22). However, breakthrough on these resins was virtually instantaneous if the aqueous solution contained as much as 250 ppm of sodium chloride, an amount commonly found in aqueous effluents. This is not entirely unexpected in that the manufacturer of these resins recommends use of salt solutions as the most effective regeneration method. Figure 11 shows the unusual breakthrough curve obtained in these tests. This curve shape can be explained by competition between the phenol and chloride ions for the hydroxide exchange sites on the resin. When the flow through the resin is started, the concentration of the two ions is small and they both exchange into the resin. As the exchange sites are filled, chloride ions exchange for phenolate ions, as well as hydroxide ions. Hence the breakthrough exceeds 100% due to an increase in concentration of phenol in the effluent above that of the influent.

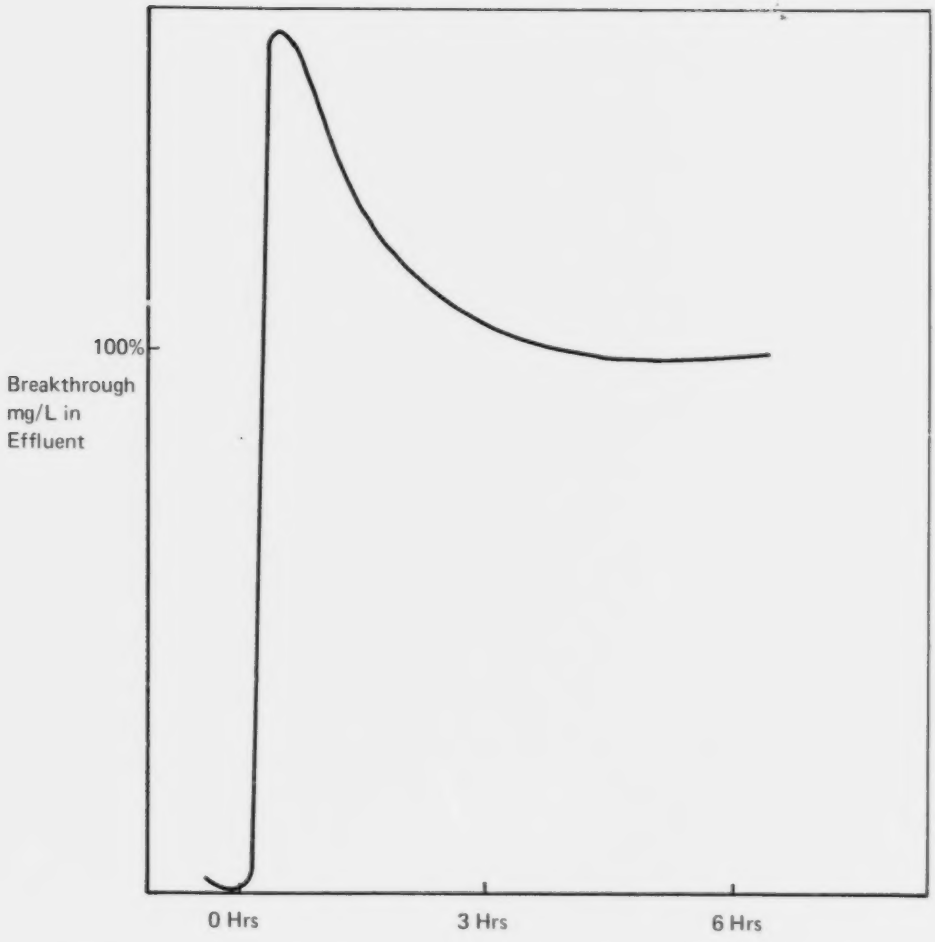


**FIGURE 11 BREAKTHROUGH CURVE OF BENZOIC ACID ON ION EXCHANGE RESIN WITH 250 ppm SODIUM CHLORIDE**

TABLE 22

$V_{50}$ Data for Polar Compounds on Ion Exchange Resins [a]

| Compound | $V_{50}$, mL/cc | |
|---|---|---|
| | IRA-904 | IRA-93 |
| Phenol | 269 | 108 |
| Benzoic Acid | 688 | 403 |

[a] Concentration: 100 mg/L (see note in text)
Column: .5 cm ID x 3.0 cm
Flow Rate: .88 - .92 mL/min

C. Design of the Full Scale Sampling Cartridge (Scale-up)

From the earlier work on sorbents, it was apparent that no single resin could be used to adequately sample a wide range of chemical classes. XAD-2 has high affinity for non-polar species but fairly low affinity for polar compounds. The best resins for adsorption of polar species were found to be the Ambersorb XE-34 series, with XE-347 exceeding the volumetric capacity of the others. Using this information, a two-stage cartridge was designed. Samples entering the cartridge would encounter the XAD-2 first. Then, any polar materials breaking through the XAD-2 would be adsorbed by the XE-347 stage.

The plans for the full scale sampling cartridge appear in Figure 12. Many factors were important in designing this system. The following discussion is intended to explain the choice of design parameters.

1. Hardware

Stainless steel was chosen for construction of the cartridge because it is chemically inert to organic species, easy to work with and rugged enough for field work. Viton A was used as the gasket material between steel surfaces as it has more dependable sealing qualities than PTFE.

The inside diameter of the cartridge was determined by the relationship between the desired sampling rate and the linear velocity criterion established in this work as a constraint for efficient collection. It was already established that this cartridge should be capable of collecting a Level 1 sample: 10L in 4 hours. This is equivalent to 42 mL/min. Also, it has been demonstrated (Section V-A above) that linear velocities of eluent greater than 4.0 cm/min produce undesirable reductions in the volumetric capacity of the column. Therefore, the cross-sectional area of the cartridge should be no smaller than

$$\frac{42 \text{ cm}^3/\text{min}}{4.0 \text{ cm/min}} = 10.5 \text{ cm}^2$$

This is equivalent to an inside diameter of 3.65 cm or 1.4 inches. With this in mind, it was decided to employ a 1.5" ID stainless steel pipe.

The minimum length of the resin bed was determined by the retention characteristics of the resins used. To obtain satisfactory uptake of the compounds (>95% efficiency), it is necessary to use sufficient resin to ensure that the 10 L of sample represent no more than 1/2 $V_{50}$ for any solute of interest. For example, to calculate the quantity of XAD-2 resin required, the compound acetophenone was used as a worst case example of a non-polar solute. $V_{50}$ for acetophenone on XAD-2 is 650 mL/cc. Therefore, 1/2 $V_{50}$ = 325 mL/cc and 10,000 mL ÷ 325 mL/cc = 30.8 cc of resin would be required. Since the cross-sectional area is 11.4 $cm^2$, the resin bed must be no shorter than 2.7 cm.

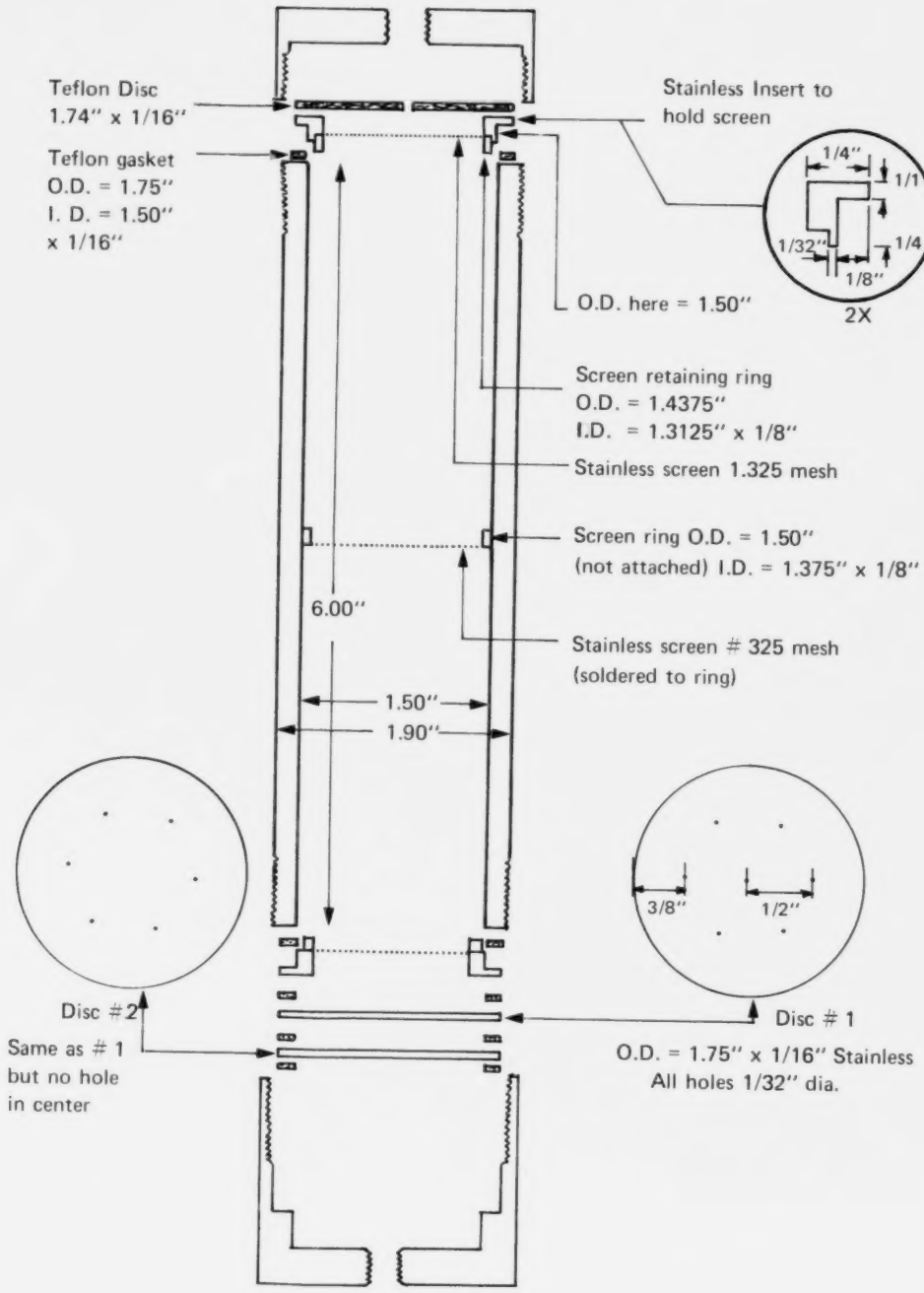


**FIGURE 12 PLAN OF SORBENT CARTRIDGE (to scale)**

It is generally accepted that an adsorbent bed should have a length-to-diameter ratio considerably greater than one, to avoid channeling and back eddy effects. The requirements for a sampling cartridge are not as severe as those for a chromatographic column. However, it was suspected that a resin bed 2.7 cm in length by 3.8 cm in diameter (ratio 0.7:1) would probably show channeling effects. For this reason the length of the cartridge was set at 15 cm, 7.5 cm for each of the two beds (approximately 2:1 length-to-diameter ratio). The cartridge was thus somewhat "overdesigned" compared to the criteria for direct scale-up from the laboratory results, and would be sufficient for collection of 30 L, as opposed to 10 L of water at the specified 42 mL/min flow rate. One disadvantage to overdesign is that the "blank" associated with the larger quantity of resin may interfere with the analysis of trace (ppb) level organics. Recoveries from the cartridge should not be significantly reduced by using the larger quantity of resin so long as the desorption solvent flow is in a counter direction to the original sample flow.

2. Flow-through Cartridge

The first thing the sample encounters as it enters the cartridge is a cavity which is filled with glass wool. The purpose of this is to remove any particulate material from the sample stream before it reaches the resin.

After the glass wool there is a system of baffle plates. These were designed to distribute the flow evenly over the entire substrate level.

Following the baffle plates the sample encounters the XAD-2 resin, followed by a stainless steel separating screen and finally the XE-347 resin. Note that the direction of flow is UP. This is thought to minimize problems due to bubbles or channeling as a result of the action of gravity on the system.

## D. Use of Full Scale Cartridge

### 1. Adsorption of Model Compounds

The first test of the full scale cartridge involved verification of predicted breakthrough behavior of a mixture of 7 model compounds. A 10L sample containing the model analytes at a concentration of 10 ppm, was passed through the sorbent cartridge in 4 hours, at a 4 cm/min linear flow rate.) Hourly samples of the effluent of the cartridge were taken in an effort to determine the extent of breakthrough. A 1/10 dilution of the feed solution measured .217 absorbance units (254 nm), whereas the effluent samples measured .000 AU. It is therefore apparent that no breakthrough occurred. This is consistent with the previous work in designing the cartridge.

Table 23 shows the recovery of 7 model compounds from each stage of the sorbent cartridge. The non-polar compounds such as trichloropropane and naphthalene were efficiently adsorbed by the XAD-2 resin, as shown by the fact that none of these compounds were recovered from the XE-347 stage. However, the more polar compounds, such as phenol and pyrrole did, in fact, breakthrough the XAD-2 stage and were trapped by the XE-347 stage.

It should be noted that the breakthrough of phenol through the XAD-2 resin is predicted by the $V_{50}$ data presented earlier. $V_{50}$ for phenol on XAD-2 has been shown to be 75 mL/cc. Since a total of 87 cc of XAD-2 resin ($3'' \times \frac{1.5''}{2} \times \pi \times (2.54)^3$) were used, 50% breakthrough for phenol in this case would occur at 6,500 mL, or only 65% of the total 10 L passed through the column.

The necessity of a two-stage design is demonstrated by the recovery of pyrrole in these batch experiments. From these data presented it appears that by extending the length of the XAD-2 portion of cartridge one could presumably trap all the phenol present in the aqueous system. However, in the case of pyrrole, XAD-2 appears to have essentially no capacity at all. Extension of the length of the cartridge could not substantially increase the recovery of this compound.

It is also interesting to see that this gross difference between the affinity of XAD-2 for phenol and pyrrole is not explained by the difference in Water-octanol partition coefficients ($P_{oct}$) of the two compounds. $P_{oct}$ for phenol is $\sim$30, while $P_{oct}$ for pyrrole is $\sim$15 (26). One possible explanation is that phenol is aromatic, while pyrrole is not. This seems to support the contention that there are multiple retention mechanisms involved with styrene-divinylbenzene copolymers.

### 2. Overall Recovery

Overall recovery of 7 model compounds was determined using the full-scale sorbent cartridge and compared to recoveries generated by solvent extracting using methylene chloride. Table 24 shows these data, which are averages for 7 and 8 determinations for the sorbent cartridge

TABLE 23

% Recovery of Model Compounds by Batch Extraction

| Compound | From XAD-2 Resin | From XE-347 Resin | Total |
|---|---|---|---|
| 1,2,3-trichloropropane | 78 | 0 | 78 |
| Naphthalene | 84 | 0 | 84 |
| Diethylphthalate | 89 | 0 | 89 |
| Acridine | 97 | 0 | 97 |
| Phenol | 47 | 27 | 74 |
| Dodecane | 17 | 0 | 17 |
| Pyrrole | 0 | 42 | 42 |

TABLE 24

% Recovery of Model Compounds by Two Methods

| Compound | Sorbent Cartridge Recovery % | SD* | % RSD** | Solvent Extraction Recovery % | SD | % RSD |
|---|---|---|---|---|---|---|
| 1,2,3-trichloropropane | 76% | 18 | 24 | 75 | 12 | 15% |
| Naphthalene | 80 | 18 | 23 | 92 | 12 | 13 |
| Diethylphthalate | 88 | 19 | 22 | 101 | 13 | 13 |
| Acridine | 99 | 15 | 16 | 89 | 21 | 23 |
| Phenol | 76 | 19 | 26 | 17 | 7 | 42 |
| Dedocane | 18 | 13 | 70 | 41 | 4 | 9 |
| Pyrrole | 57 | 24 | 43 | 46 | 9 | 20 |

* Standard Deviation
** Relative Standard Deviation

and 4 determinations for the solvent extraction. In some cases the two methods are about equal, some cases the solvent extraction is superior and other cases the cartridge method is superior. One substantial difference between the two methods is that phenol is recovered to a much higher extent using the sampling cartridge than by solvent extraction. Phenol is typically a problem compound, especially since it is a common pollutant.

At first glance the recovery of dodecane, a strongly hydrophobic compound, appears to be surprisingly quite low for both methods. However, this phenomenon is rather frequently reported for aliphatic hydrocarbons and appears to be related to the difficulty of dissolving these species in the water sample. In many cases the dodecane is not in solution at all, but exists rather as micelles and is therefore not available to be extracted.

Recovery of the remaining compounds are comparable between the two methods.

3. Effect of Solvent on Desorption from XE-347 Resin

Originally it was thought that methanol, being more polar, would be a better solvent than methylene chloride for recovery of compounds adsorbed on a polar resin (XE-347). However, it was found that the recovery of phenol using methylene chloride was 90% of the recovery obtained using methanol. For this reason, it was decided to use methylene chloride as the solvent for both resins.

4. Effect of Method of Desorption

A comparison was made between the recoveries obtained using batch extraction versus continuous extraction of compounds adsorbed in the sorbent trap (Table 25). A substantial increase in the recovery of pyrrole was obtained using the continuous extraction method. However, no significant change was noted in the recovery of the other compounds. In light of these results, and because of ease of operation, it was decided to use the continuous extractor for subsequent samples.

5. Use of Sorbent Cartridge on Environmental Sample

The full scale sorbent cartridge was used to analyze the organic content of 10 L of coke preheater scrubber water obtained from a steel manufacturing firm. Table 26 gives the data for total Chromatographic Organics and Gravimetric Organics extracted from this sample. This same sample was also subjected to a Level I solvent extraction with methylene chloride. Although the GRAV values for each method are comparable, the sorbent cartridge was capable of extracting 50% more TCO material than the solvent extraction. Figure 13 shows the chromatograms of each extract. The asterisk shows the phenol peak, confirmed by comparison of retention time with a standard sample.

TABLE 25

Recovery of Model Compounds
by Batch and Continuous Extraction

| Compound | Batch Extraction | Continuous Extraction |
|---|---|---|
| 1,2,3-trichloropropane | 78 | 70 |
| Naphthalene | 84 | 69 |
| Diethylphthalate | 89 | 86 |
| Acridine | 97 | 111 |
| Phenol | 74 | 83 |
| Dodecane | 17 | 21 |
| Pyrrole | 42 | 79 |

TABLE 26

Total Recovery of Organics from Aqueous
Effluent Sample

| | TCO, mg/L | GRAV, mg/L |
|---|---|---|
| Sorbent Cartridge | 8.9 | 47 |
| Solvent Extraction | 6.0 | 46 |

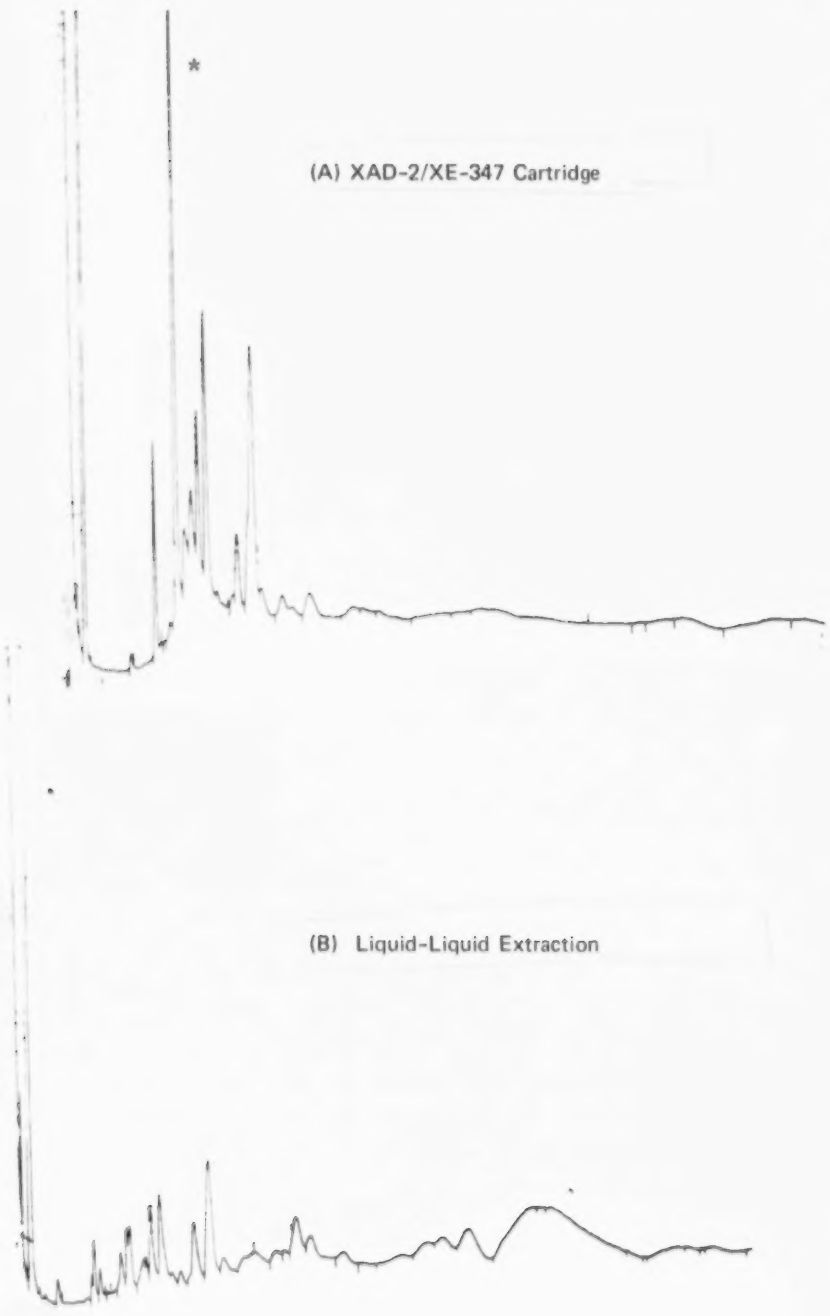


**FIGURE 13** **CHROMATOGRAMS OF ORGANICS RECOVERED FROM AQUEOUS EFFLUENT USING: (A) XAD-2/XE-347 CARTRIDGE AND (B) LIQUID-LIQUID EXTRACTION** (Each injection corresponds to the same aliquot of an original 10L aqueous sample)

## VI. CONCLUSIONS AND RECOMMENDATIONS

The chromatographic approach to characterization of sorbent-solute behavior allows rapid, simple quantitative evaluation of resins for water sampling applications. The volumetric breakthrough capacity, $V_{50}$, as determined in a small scale frontal chromatography experiment, has been shown to be a fundamental property of the sorbent-solute system. At low ($\sim$10 ppm) solute concentrations, uptake of solute by the sorbent is governed by volumetric capacity, not weight capacity, of the resin. Therefore, the collection efficiency is independent of concentration; a 10 ppb solution can be expected to breakthrough a given sorbent cartridge just as rapidly as a 10 ppm or higher.

Values of $V_{50}$ determined in small scale laboratory experiments were valuable in setting design parameters for a full-scale sampling cartridge. The use of such screening studies is highly recommended whenever it is desired to determine the optimum sampling system for a particular organic analyte is water at concentrations of 10 ppm or lower. One of the principal advantages is the ability to determine the required data which small quantities of analyte, thus minimizing worker exposure to test chemicals as well as saving time and money.

Uptake is greatly affected by the flow rate through the cartridge. Decreased collection efficiency at high sample flow rates is presumed to be due to mass transfer effects. Design criteria for full scale sampling systems therefore include a limitation on the linear (face) velocity of the sample through the cartridge. To ensure optimum, equilibrium uptake, the flow rate must be such that the face velocity (sample flow rate in mL/min divided by the cross-sectional area of the resin bed) is $\leq$4 cm/min. This constraint combines with $V_{50}$ to determine the size and shape of resin bed required for any particular sampling application.

Based on the results of screening a variety of sorbent-solute pairs, it appears that a combination of two dissimilar resins is the most promising approach to a general purpose sorbent sampling system. In particular, a combination of XAD-2 and XE-347 resins offers the possibility of collection and recovery of both non-polar and polar organic species. This XAD-2/XE-347 system was, for the most part, found to be comparable with solvent extraction in regards to recovery of model compounds. Low molecular weight, polar organic species such as phenol and pyrrole were recovered in higher yield from the cartridge. High levels of suspended particulate in the aqueous sample will require a slight modification to the sorbent cartridge and/or incorporation of a filter upstream of the sorbent bed.

The mixed bed XAD-2/XE-347 sorbent cartridge is recommended for use for general and compound-specific sampling of organics from water at levels of 10-100 ppm and below. If an aqueous stream is suspected to contain more than 100 ppm of organics or if its organic loading is unknown, the breakthrough may occur before a 10 L total sample is collected. Also, if more than 1 g of organic material is recovered from

the 3.8 cm by 15 cm XAD-2/XE-347 cartridge, the possibility that the weight capacity limitation has led to premature breakthrough should be considered.

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## APPENDIX A

### Theoretical Considerations of $V_{50}$

This Appendix presents a derivation from chromatographic principles to demonstrate that the $V_{50}$ point on a frontal chromatogram is independent on the shape of the front. This $V_{50}$ point is not affected by deviations from ideal behavior (i.e. instantaneous equilibrium) under the actual experimental conditions, and is, therefore, a fundamental characteristic of the sorbent-sorbate system.

If an adsorbent bed were challenged with a solution containing one analyte, a breakthrough curve similar to Figure A-1 would be generated assuming ideal conditions (instantaneous equilibrium). The volume $V_T$ is given the name threshold or retention volume by, among others, Wilson (52) and DeVault (15). This volume of solution is a characteristic of the particular sorbent/solute system, and is, therefore, of particular interest in examination of this system.

If the constraint of instantaneous equilibrium is removed, a breakthrough curve similar to Figure A-2 is generated. The characteristic value, $V_T$, of Figure A-1 is no longer easily recognizable. However, as shown by Glueckauf and Coates (20) the $V_T$ value is still readily determinable from the breakthrough curve. The value $V_T$, as will be shown, corresponds to the value $V_{50}$, the volume at the 50% breakthrough point.

Let the following symbols be defined as:

$q$ •≡• the amount of solute adsorbed by the resin per unit of mass of resin

$f$ •≡• the equilibrium amount of solute adsorbed by the resin per unit mass of resin, i.e., the adsorption isotherm for the solute/resin system

$v$ •≡• the volume of solution being passed through the system

$c$ •≡• the amount of solute in the mobile phase per unit volume of mobile phase

$c^\circ$ •≡• the initial amount of solute in the mobile phase per unit volume of mobile phase, i.e., the feed or challenge concentration

$x$ •≡• the distance of any point in the resin measured in grams of resin

$\alpha$ •≡• the void volume of the resin per unit mass of resin

Now, consider a cross-sectional slice of the column with thickness $\delta x$, such that $\frac{\partial c}{\partial x}$, $\frac{\partial c}{\partial v}$ and $\frac{\partial q}{\partial v}$ are all constant over the entire slice. $\frac{\partial c}{\partial x}$ is

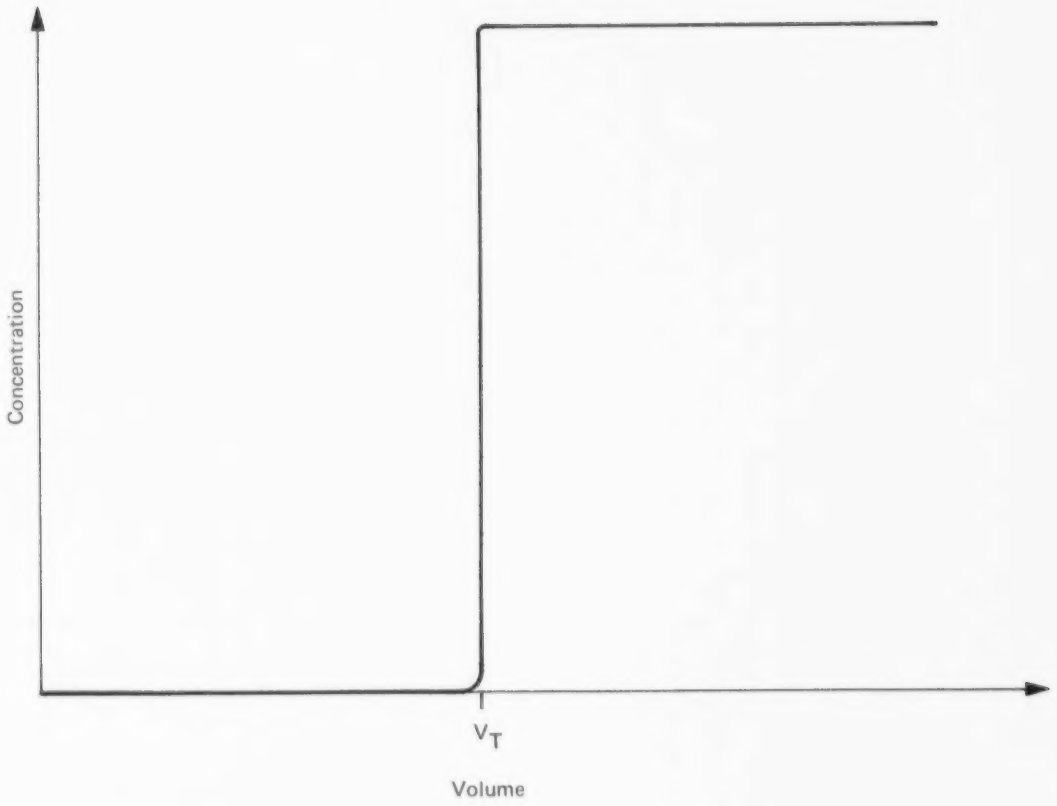



FIGURE A-1 BREAKTHROUGH CURVE FOR ONE SOLUTE, ASSUMING INSTANTANEOUS EQUILIBRIUM

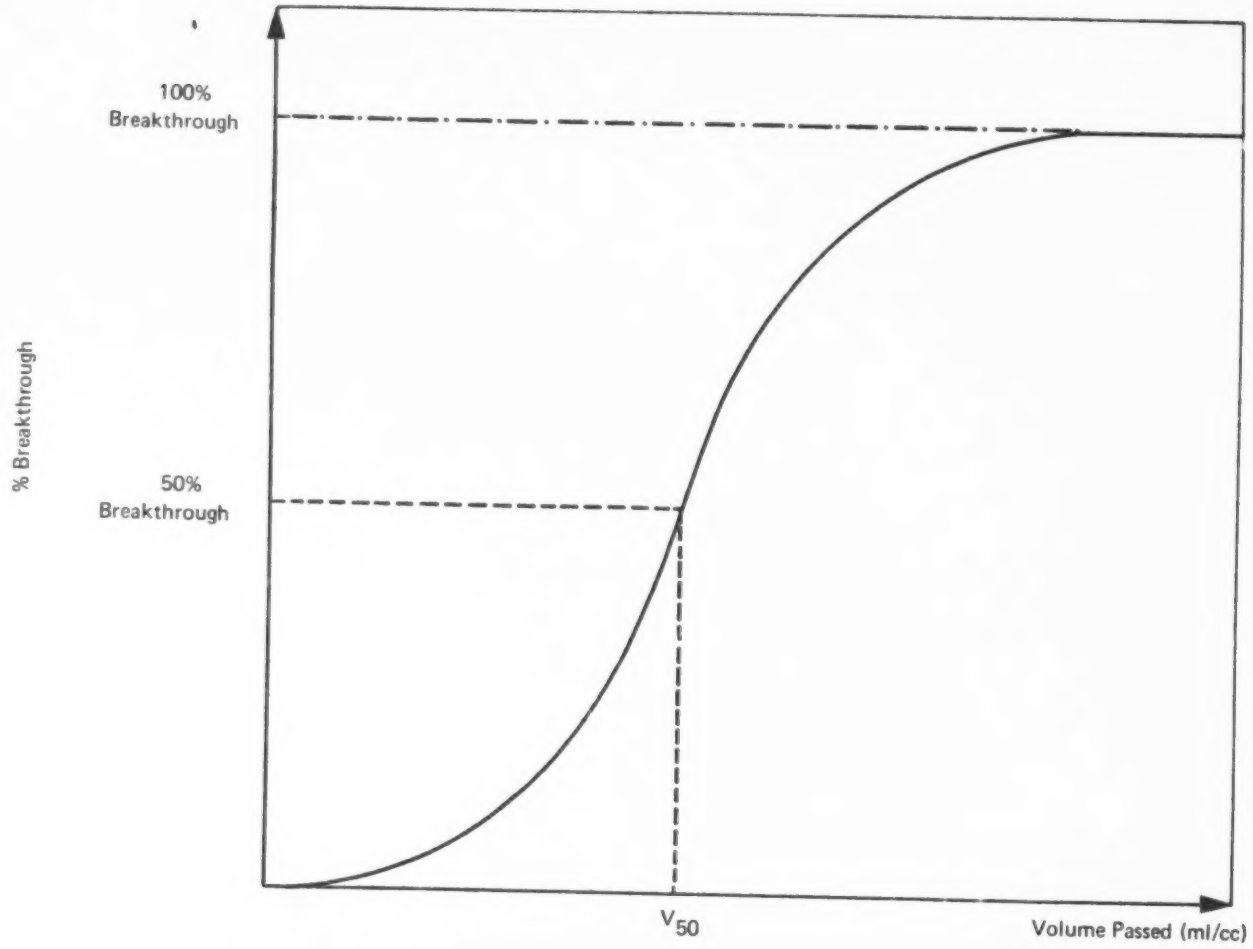



FIGURE A-2 A BREAKTHROUGH CURVE

the difference in concentration between the beginning and end of the slice, i.e., the concentration gradient of the slice. When a small volume, $\delta v$, of solution is passed into this region the solute is distributed in various ways: The quantity $(\frac{\partial c}{\partial x}\ \delta x)\ \delta v$ represents the amount of solute by which the solution leaving the slice exceeds that amount entering the slice; the quantity $\alpha\delta x(\frac{\partial c}{\partial v}\ \delta v)$ represents the amount of solute in solution (i.e., trapped in the dead volume portion) inside this slice and; the quantity of solute <u>added to</u> the resin in this section is described by $\delta x\ (\frac{\partial q}{\partial v}\ \delta v)$. Now, by setting the sum of these equal to zero to conserve matter, and cancelling out $\delta x$ and $\delta v$ we obtain equation A-1.

$$\frac{\partial c}{\partial x} + \alpha\frac{\partial c}{\partial v} + \frac{\partial q}{\partial} = 0 \qquad \text{A-1}$$

Since $\frac{dq}{dv} = \frac{dq}{dc} \cdot \frac{dc}{dv}$ and since $(\frac{dv}{dx})_c = \frac{\frac{-\partial c}{\partial x}}{\frac{\partial c}{\partial v}}$, or $\frac{\partial c}{\partial x} = -(\frac{dv}{dx})_c\ \frac{\partial c}{\partial v}$ substitution in Equation A-1 yields:

$$(\frac{dv}{dx})_c = \alpha + \frac{dq}{dc} \qquad \text{A-2}$$

If an equilibrium condition were to exist, the quantity q could be replaced by f giving:

$$(\frac{dv}{dx})_c = \alpha + \frac{df}{dc} \qquad \text{A-3}$$

where (f-q)is the amount of solute not adsorbed due to disequilibrium. Note that both equations A-2 and A-3 are a description of the movement of a point of constant concentration (e.g., a boundary) through the column.

Once this boundary has passed a slice of the column, there exists a steady state, governed by the equilibrium isotherm, f. A certain volume dv passed into the slice contains $dvc^\circ$ mg of solute. This quantity is then distributed into either the dead volume, $\alpha dxc^\circ$, or onto the resin $f_{c^\circ}dx$. Hence we obtain:

$$c^\circ dv = \alpha dxc^\circ + fc^\circ dx \qquad \text{A-4}$$

for the steady state slice of resin. Rearranging:

$$\frac{dv}{dx} = \alpha + \frac{fc^\circ}{c^\circ} \qquad \text{A-5}$$

and combining A-5 and A-2, we obtain:

$$\frac{dq}{dc} = \frac{fc^\circ}{c^\circ} \qquad \text{A-6}$$

The quantity dq can be approximated, from A-7, assuming a first order reaction rate:

$$\frac{dq}{dt} = K(fc - q) \qquad \text{A-7}$$

where $K = D/\eta d^2$ (D is the diffusion constant, d is the particle diameter and $\eta$ is a constant dependent on the particle geometry).

Therefore, by solving A-7 for dq, combining with A-6 and replacing dt with F/dv, where F is the flow rate, we obtain:

$$dc = \frac{K}{F}(fc \cdot \frac{c^\circ}{f^\circ} - c)\, dv \qquad \text{A-8}$$

For the purposes of this discussion, we will assume that the isotherm (f) is of the Langmuir type. This gives

$$f(c) = \frac{ac}{1+bc} \qquad \text{A-9}$$

where a and b are constants.

Substituting A-8 into A-9, we obtain

$$\frac{dc}{dv} = \frac{K}{F}\left[\frac{ac}{1 + bc} \cdot \frac{c^\circ}{\left(\frac{ac^\circ}{1 + bc^\circ}\right)} - c\right] \qquad \text{A-10}$$

Simplifying:

$$\frac{dv}{dc} = \frac{F}{K}\left[\frac{1}{bc(c^\circ - c)} + \frac{1}{c^\circ - c}\right] \qquad \text{A-11}$$

or

$$\frac{dc}{dv} = \frac{K}{F}\left[\frac{bc(c^\circ - c)}{1 + bc}\right] \qquad \text{A-12}$$

To find the minima/maxima of the breakthrough curve, we set A-12 equal to 0. So,

$$0 = bc(c^\circ - c) \qquad \text{A-13}$$

Therefore, minima/maxima occur at $c = 0$ or $c = c^\circ$.

More importantly, however, the position of the inflection point in the breakthrough curve can be determined.

Differentiating A-12, we obtain:

$$\frac{d^2c}{dv^2} = \frac{bK}{F}\left[\frac{c^\circ - c}{1 + bc} + \frac{(-1)c}{1 + bc} + \frac{(-1)(b)c(c^\circ - c)}{(1 + bc)^2}\right]\frac{dc}{dv} \qquad \text{A-14}$$

Setting $\frac{d^2c}{dv^2} = 0$, we obtain

$$0 = \frac{c^\circ - c - c}{1 + bc} + \frac{(-bc)(c^\circ - c)}{(1 + bc)^2} \qquad \text{A-15}$$

then, $$bc^2 - 2c + c^\circ = 0 \qquad \text{A-16}$$

If the solution is dilute, $c^2$ is small compared to both c and $c^\circ$ so that $c = \frac{c^\circ}{2}$ (i.e., the 50% breakthrough point) is the inflection point.

Note that this point is independent of the value of either a or b in the Langmuir Isotherm (A-9). This indicates that as long as the isotherm is Langmuir, the 50% breakthrough point is the characteristic point on the breakthrough curve.

To further demonstrate this concept, we integrate Equation A-11

$$\int_{v_{\frac{c^\circ}{2}}}^{v_c} dv = \frac{F}{K}\int_{\frac{c^\circ}{2}}^{c}\left(\frac{dc}{bc(c^\circ - c)} + \frac{dc}{(c^\circ - c)}\right) \qquad \text{A-17}$$

so that,

$$v_c - v_{\frac{c^\circ}{2}} = -2.303\,\frac{F}{K}\left(\frac{1}{bc^\circ}\log\left(\frac{c^\circ - c}{c}\right) - \log 2\left(\frac{c^\circ - c}{c^\circ}\right)\right) \qquad \text{A-18}$$

Note again that it is the 50% breakthrough point, or $c/c^\circ = 0.5$, that is constant for the system, regardless of the shape of the breakthrough front. It is for this reason that this point is used in characterization of retention for sorbent/sorbate pairs.

A plot of $\frac{c}{c^\circ}$ versus $-K(v_c - v_{\frac{c^\circ}{2}})/2.3F$ is shown in Figure A-3 for two different values of $bc^\circ$.

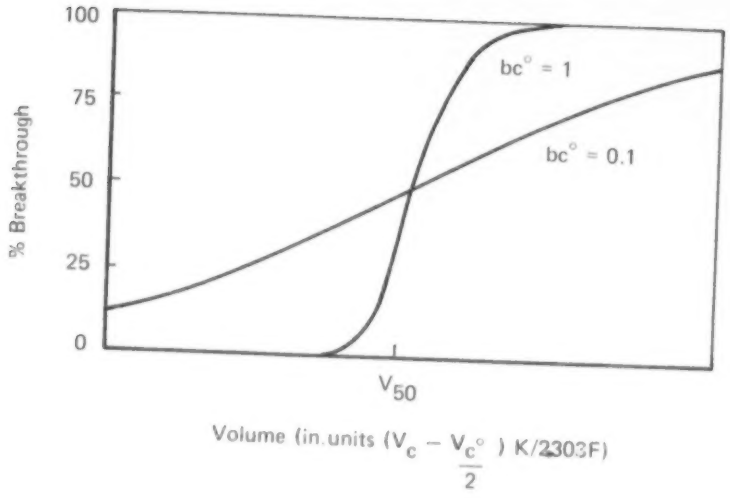



FIGURE A-3 THEORETICAL BREAKTHROUGH CURVES FOR DIFFERENT VALUES OF $bc^\circ$, ILLUSTRATING CONSTANCY OF $V_{50}$ POINT (ADAPTED FROM REFERENCE 23)

# APPENDIX B

## Physical Properties of Sorbents

Table B-1 presents some important physical constants of some macroreticular resin adsorbents.

TABLE B-1

Physical Constants of Macroreticular Resins

| Resin | Specific Surface Area $m^2/g$ | Cumulative Pore Volume cc/g | Average Pore Size, Å |
|---|---|---|---|
| XAD-2 | 330 | .89 | 90 |
| XAD-4 | 750 | 1.15 | 50 |
| XAD-7 | 450 | * | 80 |
| XAD-8 | 140 | .711 | 250 |
| XE-340 | 400 | .34 | 100** |
| XE-347 | 350 | .41 | 100** |
| XE-348 | 500 | .58 | 100** |

*Not Available

**Rough estimate from incremental pore volume plot.

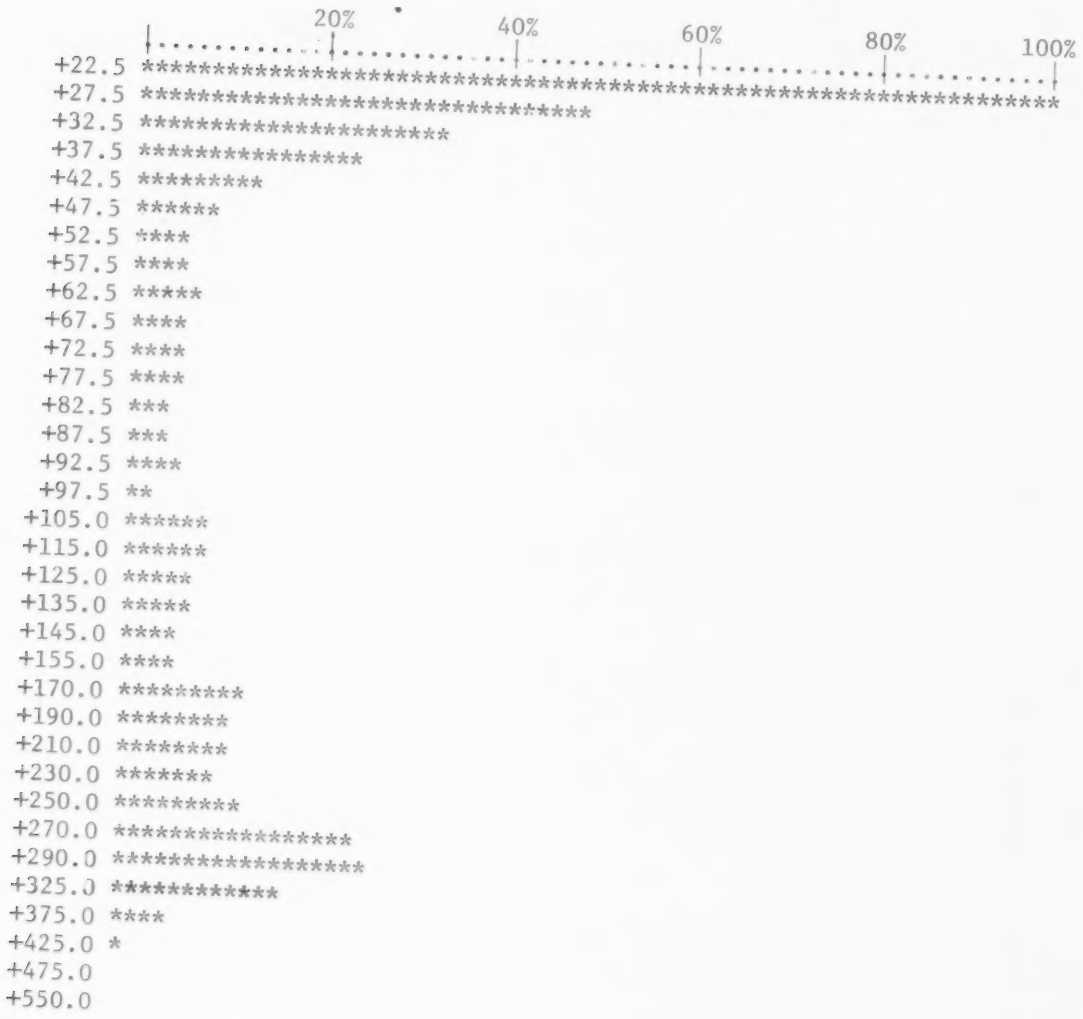
Figures B-1 through B-10 show incremental surface area and incremental pore volume plots for the following resins: XAD-2, XAD-4, XAD-8, XE-340, XE-347.

MICROMERITICS INSTRUMENT CORPORATION
DIGISORB 2500

Sample: ADL XAD-2 STA: 2 EQTIME: 3 MODE: 5 METHOD: 4

Incremental Surface Area Distribution (Desorption)

% of Maximum Surface Area (+64.753 cc/g)
Versus Average Pore Diameter, Angstroms



MICROMERITICS INSTRUMENT CORPORATION
DIGISORB 2500

Sample: ADL XAD-2 STA: 2 EQTIME: 3 MODE: 5 METHOD: 4

Incremental Surface Area Distribution (Desorption)

% of Maximum Pore Volume (+0.131443 cc/g)
Versus Average Pore Diameter, Angstroms

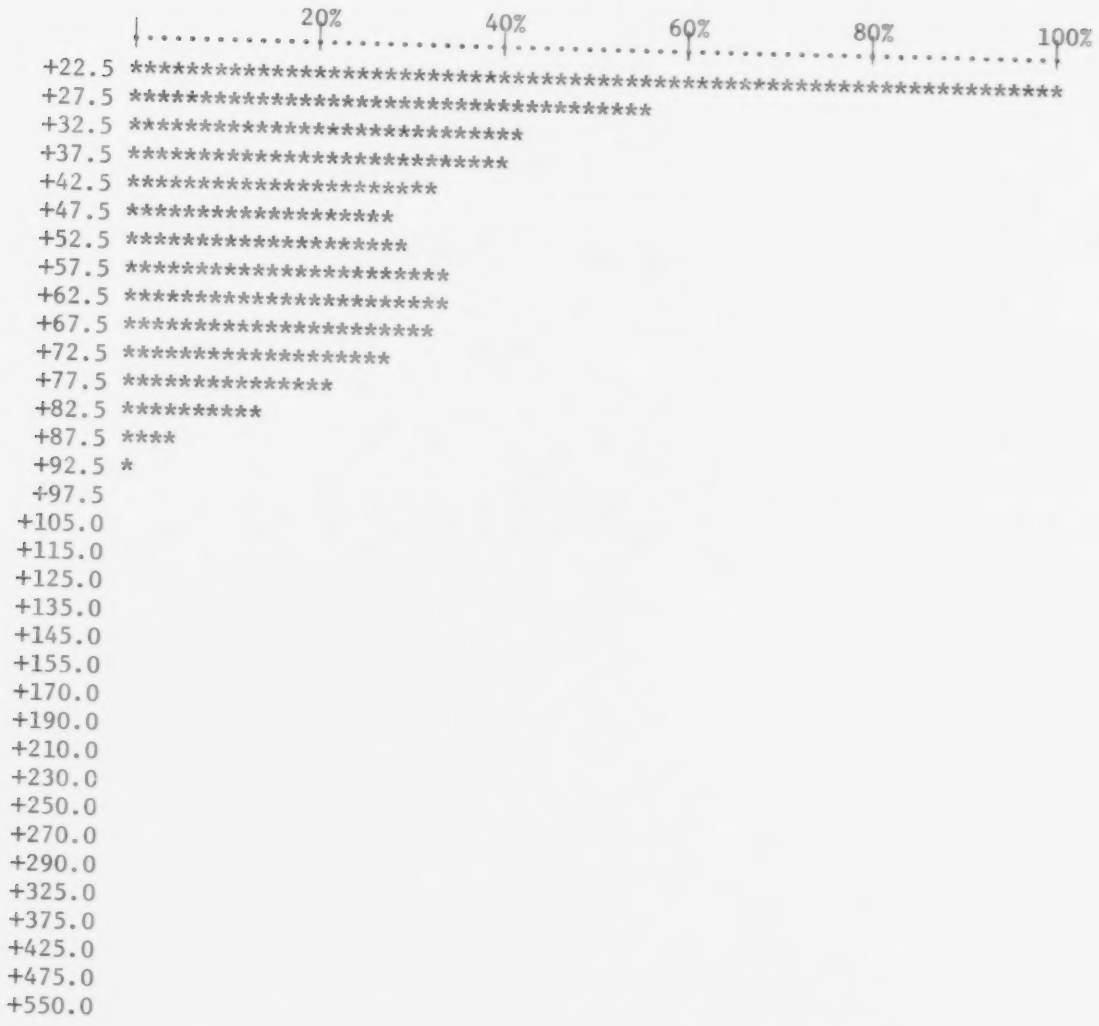
```
+22.5 ******************
+27.5 ***********
+32.5 *********
+37.5 *******
+42.5 *****
+47.5 ****
+52.5 ****
+57.5 ***
+62.5 ****
+67.5 ****
+72.5 ***
+77.5 ****
+82.5 ***
+87.5 ****
+92.5 ****
+105.0 *******
+115.0 ********
+125.0 ********
+135.0 ********
+145.0 ********
+155.0 *******
+170.0 **********************
+190.0 ********************
+210.0 ***********************
+230.0 ********************
+250.0 ******************************
+270.0 ************************************************************
+290.0 ************************************************************************
+325.0 ********************************************************************************
+375.0 ******************************************
+425.0 ******************
+475.0 ******
+550.0 *
```

MICROMERITICS INSTRUMENT CORPORATION
DIGISORB 2500

Sample: ADL XAD-4 STA: 4 EQTIME: 3 MODE: 5 METHOD: 4

Incremental Surface Area Distribution (Desorption)

% of Maximum Surface Area (+217.774 cc/g)
Versus Average Pore Diameter, Angstroms

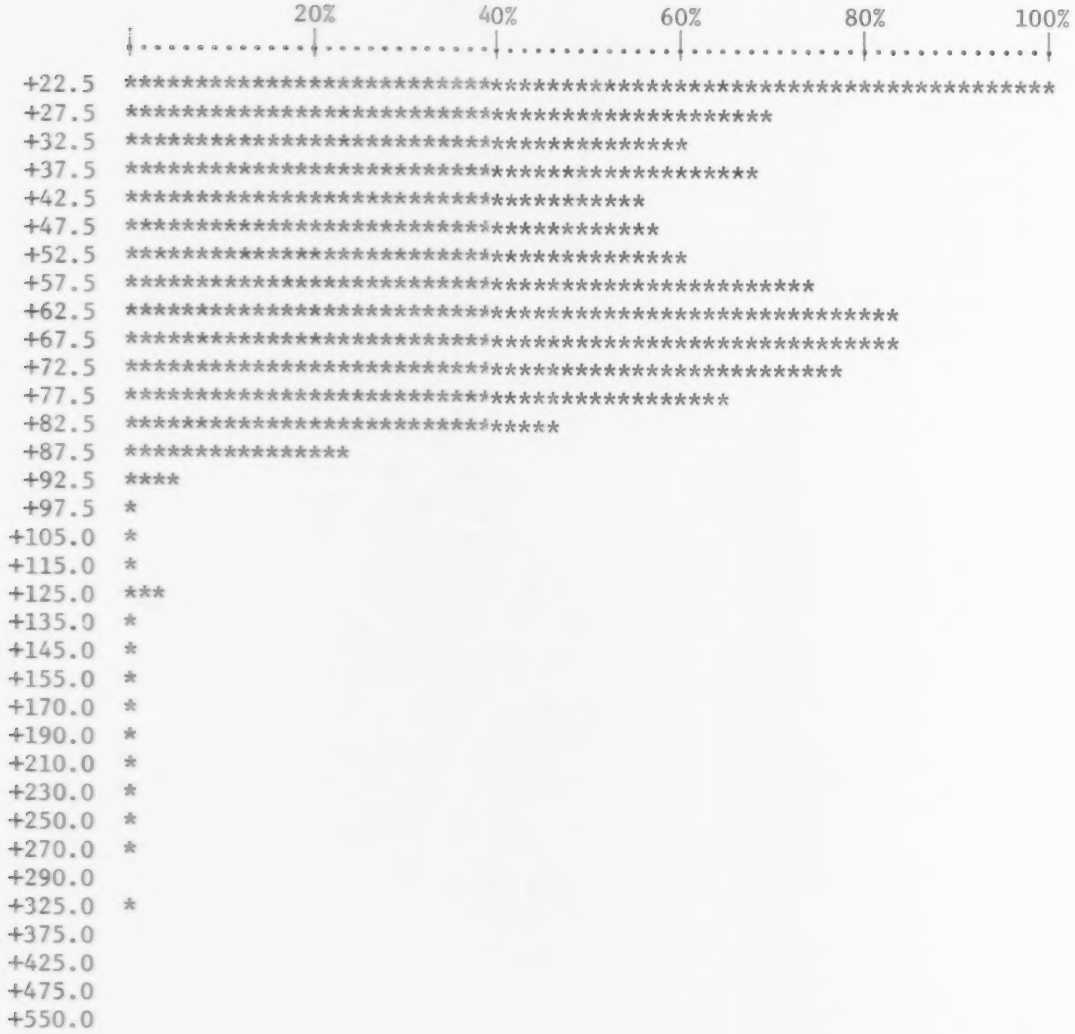


MICROMERITICS INSTRUMENT CORPORATION
DIGISORB 2500

Sample: ADL XAD-4 STA: 4 EQTIME: 3 MODE: 5 METHOD: 4

Incremental Surface Area Distribution (Desorption)

% of Maximum Pore Volume (0.122498 cc/g)
Versus Average Pore Diameter, Angstroms

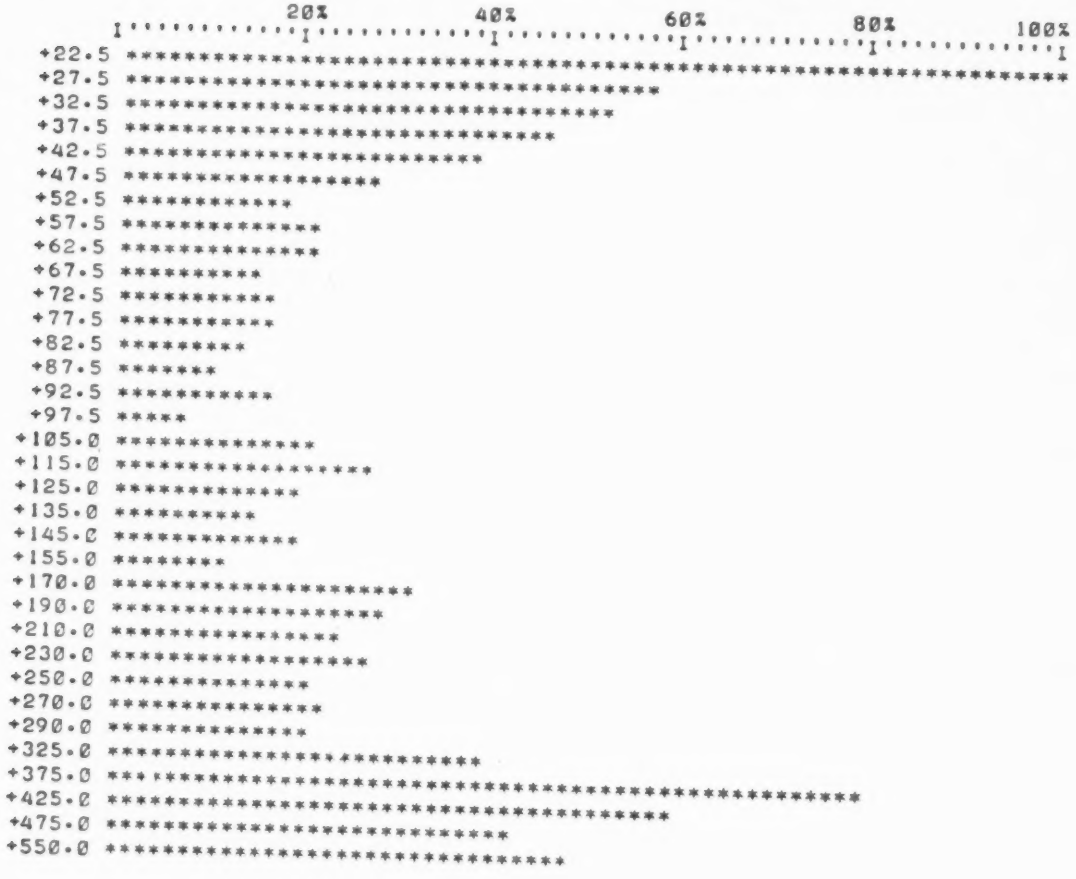


MICROMERITICS INSTRUMENT CORPORATION
DIGISORB 2500

SAMPLE:ARTHUR D. LITTLE XAD-8 STA: 1 EQTIME: 3 MODE: 5 METHOD: 3

INCREMENTAL SURFACE AREA DISTRIBUTION (DESORPTION)

% OF MAXIMUM SURFACE AREA( +14.730 SQ M/G)
VERSUS AVERAGE PORE DIAMETER, ANGSTROMS



MICROMERITICS INSTRUMENT CORPORATION
DIGISORB 2500

SAMPLE:ARTHUR D. LITTLE INC XE-347 STA: 1 EQTIME: 3 MODE: 5 METHOD: 3

INCREMENTAL PORE VOLUME DISTRIBUTION (DESORPTION)

% OF MAXIMUM PORE VOLUME( +0.057581 CC/G)

VERSUS AVERAGE PORE DIAMETER, ANGSTROMS

MICROMERITICS INSTRUMENT CORPORATION
DIGISORB 2500

SAMPLE:ARTHUR D. LITTLE INC XE-347 STA: 1 EQTIME: 3 MODE: 5 METHOD: 3

INCREMENTAL SURFACE AREA DISTRIBUTION (DESORPTION)

% OF MAXIMUM SURFACE AREA( +72.688 SQ M/G)

VERSUS AVERAGE PORE DIAMETER, ANGSTROMS

```
      I'''''''''''I'''''''''''I'''''''''''I'''''''''''I'''''''''''I
      20%        40%        60%        80%        100%
 +22.5 ************************************************************
 +27.5 ************************************************************
 +32.5 ***************************
 +37.5 **************
 +42.5 *******
 +47.5 **
 +52.5 *
 +57.5 *
 +62.5 *
 +67.5
 +72.5 *
 +77.5 *
 +82.5
 +87.5 *
 +92.5 *
 +97.5
+105.0 *
+115.0 **
+125.0 *
+135.0 *
+145.0 **
+155.0 **
+170.0 *****
+190.0 ******
+210.0 ******
+230.0 *********
+
 250.0 *******
+270.0 *****
+290.0 ***
+325.0 ****
+375.0 *
+425.0
+475.0
+550.0
```

MICROMERITICS INSTRUMENT CORPORATION
DIGISORB 2500

SAMPLE:ARTHUR D. LITTLE XE-340 STA: 2 EQTIME: 3 MODE: 5 METHOD: 3

INCREMENTAL SURFACE AREA DISTRIBUTION (DESORPTION)

% OF MAXIMUM SURFACE AREA( +37.022 SQ M/G)
VERSUS AVERAGE PORE DIAMETER, ANGSTROMS

```
                  20%          40%          60%          80%          100%
      I'''''''''''I''''''''''''I''''''''''''I''''''''''''I''''''''''''I
+22.5 ************************************************************************
+27.5 *********************************
+32.5 ************
+37.5 *********
+42.5 *******
+47.5 **
+52.5 *
+57.5 *
+62.5 *
+67.5
+72.5 *
+77.5 *
+82.5 *
+87.5 *
+92.5 *
+97.5
+105.0 *
+115.0 ***
+125.0 **
+135.0 **
+145.0 ****
+155.0 **
+170.0 *******
+190.0 ********
+210.0 ********
+230.0 ************
+250.0 **********
+270.0 *********
+290.0 ***********
+325.0 ****************
+375.0 *******
+425.0 *
+475.0
+550.0
```

MICROMERITICS INSTRUMENT CORPORATION
DIGISORB 2500

SAMPLE:ARTHUR D. LITTLE XE-340 STA: 2 EQTIME: 3 MODE: 5 METHOD: 3

INCREMENTAL PORE VOLUME DISTRIBUTION (DESORPTION)

% OF MAXIMUM PORE VOLUME( +0.075190 CC/G)
VERSUS AVERAGE PORE DIAMETER, ANGSTROMS

```
                20%          40%          60%          80%          100%
     I'''''''''''I''''''''''''I''''''''''''I''''''''''''I''''''''''''I
 +22.5 ******************
 +27.5 ************
 +32.5 *****
 +37.5 ****
 +42.5 ****
 +47.5 *
 +52.5 *
 +57.5 *
 +62.5 *
 +67.5
 +72.5 *
 +77.5 *
 +82.5 *
 +87.5 *
 +92.5 *
 +97.5
+105.0 **
+115.0 ****
+125.0 ***
+135.0 ***
+145.0 ******
+155.0 ****
+170.0 ***************
+190.0 ******************
+210.0 ***********************
+230.0 ****************************************
+250.0 *********************************
+270.0 *********************************
+290.0 ****************************************
+325.0 ********************************************************************************
+375.0 *********************************
+425.0 ******
+475.0
+550.0
```

MICROMERITICS INSTRUMENT CORPORATION
DIGISORB 2500

SAMPLE:ARTHUR D. LITTLE XAD-8 STA: 1 EQTIME: 3 MODE: 5 METHOD: 3

INCREMENTAL PORE VOLUME DISTRIBUTION (DESORPTION)

% OF MAXIMUM PORE VOLUME( +0.109549 CC/G)
VERSUS AVERAGE PORE DIAMETER, ANGSTROMS

```
                20%          40%          60%          80%          100%
    I.....I.....I.....I.....I.....I.....I.....I.....I.....I.....I
+22.5 *****
+27.5 ***
+32.5 ****
+37.5 ****
+42.5 ****
+47.5 ***
+52.5 **
+57.5 ***
+62.5 ***
+67.5 **
+72.5 ***
+77.5 ***
+82.5 **
+87.5 **
+92.5 ***
+97.5 **
+105.0 *****
+115.0 *******
+125.0 ******
+135.0 *****
+145.0 ******
+155.0 ****
+170.0 ***********
+190.0 ***********
+210.0 ***********
+230.0 **************
+250.0 ***********
+270.0 ************
+290.0 **************
+325.0 ******************************
+375.0 ************************************************************************
+425.0 ************************************************************
+475.0 ********************************************
+550.0 ********************************************************************
```